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Plasma Processing of Materials

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The report contains an assessment of recent developments in processing materials through the use of plasma technology. Advances in this field in foreign countries are discussed and the potentials for this type of processing relative to selected materials from the standpoints of cost-effectiveness and technical viability made. It addresses thermal plasma melting and remelting technology, extracting and refining technology, plasma deposition, thermal plasma synthesis and consolidation and processing using low-pressure nonequilibrium plasmas. Conclusions and recommendations are made for potential research and development projects in each of the technologies studied.

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8. Melting & Refining of Superalloys,
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PLASMA PROCESSING OF MATERIALS

Report of
The Committee on Plasma Processing of Materials

NATIONAL MATERIALS ADVISORY BOARD
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ABSTRACT

A National Research Council committee was formed to study recent developments in processing materials through the use of plasma technology. Noteworthy advances in this field have occurred in several foreign countries, and great promise is shown for a number of new and improved methods for materials systems. The study addresses thermal plasma melting and remelting technology, extracting and refining technology, plasma deposition, thermal plasma synthesis and consolidation, and processing using low-pressure nonequilibrium plasmas. Opportunities based on these technologies are discussed, and priorities for support of research and development are suggested.

The committee points out that thermal plasma processing technology in the United States has generally not advanced beyond laboratory-scale or pilot-plant stages. In contrast, large-scale production facilities have been developed in the Soviet Union, the German Democratic Republic, and Japan. Significant advances in some specialized areas have also been achieved in several European countries, Canada, and South Africa. The United States, on the other hand, is at the leading edge of the processing science and technology associated with the application of low pressure plasmas as employed especially in the electronics industry.

The committee concludes that there would be a substantial payoff from funds devoted to research and development, with the most promising being perhaps the area of plasma deposition processing as it relates to microelectronics and very-large-scale integrated circuits. Specific suggestions are given for research and development projects in each of the technologies studied.

PREFACE

Plasma processing of materials is the practical employment of two interrelated disciplines--plasma chemistry and arc technology. Both fields make use of the plasma state of matter, wherein a plasma, made up of a mixture of neutral particles, ions, and electrons, can potentially be utilized for producing new materials with unusual, superior properties, for developing new chemical compounds and processes, and for altering and refining materials and surfaces. This potential, a part of which has already been realized, can play a significant role in the future of materials science and engineering endeavors.

These possibilities have been recognized in several foreign countries, and notably Japan, the Soviet Union, and the German Democratic Republic have taken lead roles in pioneering the exploitation of plasma processing science and technology for their national needs.

With the growing awareness in the United States that plasma processing promises a broad range of new and improved processing operations for materials systems, the Department of Defense and the National Aeronautics and Space Administration requested the National Research Council to study this subject in a broad, fundamental manner. Such a study would assist in organizing the information presently available about the field, in assessing its specific importance to materials science and engineering, and in providing a perspective for future investigations.

The Committee on Plasma Processing of Materials was formed by the National Materials Advisory Board (NMAB) to study the areas of materials science and engineering processing of materials pertinent to:

- The unique aspects of utilizing plasmas for materials processing
- The use of thermal plasma for melting and remelting technology
- The technological opportunities in extractive metallurgy
- Spray deposition for near-net-shape manufacturing
- Thermal plasma synthesis and consolidation (e.g., the production of submicron oxide powders, synthesis of ternary carbides and nitrides, plasma sintering of ceramic materials, and the spheroidization and densification of porous particles and conglomerates)
- The potential for processing materials using low-pressure, nonequilibrium plasmas

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The committee was asked to provide an overview of the various technological opportunities in plasma processing and to suggest the kind and extent of research and development necesary to advance plasma processing technology.

In carrying out its assignment the committee examined all technical and scientific aspects of plasma processing. It benefited from the experience of many people engaged in the field, both in the United States and abroad, through examination of their writings and through personal contacts and discussion. Although the committee did not go deeply into the complex legal and economic issues of certain aspects of plasma processing, it was keenly aware of these nontechnical factors.

This report presents the committee's findings based on extensive deliberations during its review and distillation of a large body of information.

ACKNOWLEDGMENTS

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CONTENTS

Chapter 1

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

INTRODUCTION

The plasma processing of materials is an important, growing field, which
encompasses a broad range of activities, ranging from the production of
electronic materials, deposition and coating technologies, to the synthesis of
uniformly sized powders and compounds, and the melting-refining of
superalloys, titanium and other important engineering materials. These
operations will have a continuing impact on both our defense related
industries and on our industrial society as a whole.

The purpose of this report is to provide a critical assessment of the
principal current and anticipated activities in the plasma processing field
with emphasis on the technological engineering opportunities that are
available for exploration and the research needs that have to be met in order
that these opportunities may be realized. In this context, the principal
conclusions and recommendations of this report follow.

CONCLUSIONS

1.   In melting and remelting, the plasma process provides the potential
for efficient processing and recycling of scrap and alloy materials, thus
conserving both hydrocarbon fuels and critical materials. Systems exceeding
20-MW capacity are in operation in a number of foreign countries, processing
high-quality steels and other materials. The process also permits achieving
unique materials, such as the tungsten monocrystals with room-temperature
ductility.

2.   Few full-scale plasma installations for metal extraction have been
constructed; nonetheless, the technological feasibility of using plasma
reactors for the extraction of metals from their ores is established.
Demonstration plants have been or are being constructed in foreign countries
for the melting of ferrous scrap, sponge iron production, and the production
of ferrochrome. Important technological opportunities for plasma extractive
metallurgy include the production of magnesium, titanium, tungsten, other
refractory metals, and possibly aluminum. The processing of fly ash for the
recovery of aluminum, titanium, and other constituents is a longer range
possibility.

3.   By injection of prealloyed powder particles into a thermal plasma (either in inert gas or in a reduced pressure environment) one can obtain rapidly solidified metastable (i.e., amorphous, microcrystalline, and supersaturated solid solution) bulk structures or thin coatings. These developments can be applied to the processing of near-net shapes, graded structures, and composites using mixed powder feeds, gas-injection techniques or multiple source systems. By selecting a proper injection mode of organo-metallic precursors, one can control the residence time and hence the decomposition pathways so as to generate continuous films (chilled substrates) or fine particulates. This concept of decoupling of heating and residence time in the plasma is also applicable to systems involving particulate injection, as in refining metals and ores.

4.   The most important development in the area of plasma synthesis and in consolidation is the preparation of metal and ceramic powders and their mixtures. The major impact of this technology of submicron powder processing is expected to occur within about 10 years. Of particular interest is the preparation of submicron ceramics, especially SiC and Si_3N_4 from halide and organometallics which in dense form are candidate materials for advanced heat engines applications.

5.   A large and growing area of application of nonequilibrium plasmas is in the fabrication of integrated circuits and thus is an area of vital importance to our electronics industry. Applications utilizing noble gas plasmas, such as ion-plating, sputter-deposition of thin films and sputter-etching for pattern generation, while numerous and significant, are based on relatively well-understood phenomena and probably will not benefit substantially from additional basic research. Applications utilizing molecular gas plasmas, where reactive species are generated in situ, such as plasma etching and plasma-enhanced chemical vapor deposition, are based on phenomena that are not well-understood in the fundamental sense. Consequently, much of the development for these applications has been done by empirical, trial and error methodology. Timely research and development in reactive plasmas is imperative to maintain a strong competitive position and for progress in high-technology industries in the United States.

RECOMMENDATIONS

From a broad perspective, the United States is lagging behind a number of nations in thermal plasma research and development. Notable among the countries that are ahead of the United States are the Soviet Union, Japan, and East German. In these countries, emphasis has been toward innovation in technology. In all cases the common factor has been recognition by these governments that plasma processing can be advantageous to their nations. Potential specific advantages for the United States include better use of strategic materials, near-net-shape processing, and processing of refractory powders. Research and development work in the United States on thermal plasma processing should be undertaken with goals such as these in mind.

Basic and innovative research is urgently recommended in the areas listed below:

1.   The poor basic understanding of the kinetic and transport phenomena in plasma systems (both thermal and nonequilibrium) is a major barrier to full

development of these processes in the United States. Experimental and analytical studies should be undertaken on kinetics and transport phenomena in plasma systems to obtain a better understanding of the electromagnetic force field, the fluid flow field and temperature fields in plasma systems including plasma-particle and plasma-surface interactions.

2. Improved diagnostic techniques are needed to measure key plasma and plasma/materials parameters. The most important advances needed are for rapid determinations of temperature and velocity fields within the plasma. Identification of species and chemical reactions are essential to the understanding of the processes. A consideration of the transport properties is also critical since the plasma may be radically changed by vaporized and/or reactive species. If such properties are provided from good experimental data, meaningful modeling and scaling can be accomplished.

3. Modeling studies are needed of the complex heat transfer, transport properties, and reactive kinetics--including plasma heat source, and molten pool ingot-crucible interface. Similarly, experimental and mathematical modeling studies are needed of the mechanics of momentum and heat transfer between the plasma and injected particles.

4. Basic research needs in nonequilibrium plasma processing that must be addressed are: characterization and understanding of the plasma environment with respect to chemical composition and the energy distributions of ions, electrons and neutrals; characterization and understanding of plasma-surface interactions especially in the area of synergistic phenomena involving energetic charged particles and neutral reactants; understanding how materials properties relate to the plasma conditions present during their formation.

5. Needed research on process innovation in low pressure plasma includes: continued development of plasma-assisted etching for very-large-scale integration (VLSI); refinement of processes for the deposition of hydrogenated amorphous silicon; extension of plasma etching and plasma deposition techniques to other solid-state technologies. Because reactive plasmas represent the least understood facet of nonequilibrium plasmas, they offer the promise of uncovering many new and attractive applications.

Efforts should be made to focus basic research on thermal and nonequilibrium plasma processing at universities, with a view to establishing in the long term a few Centers of Excellence covering all relevant aspects of the subject. A possible mechanism might be an NSF Engineering Center.

Engineering studies need to be conducted in parallel with the proposed basic research programs; presumably these will be conducted largely by industry. As an example, engineering development needs in plasma extractive metallurgy include the establishment of design criteria for plasma systems to obtain the appropriate scale of operation, the residence time, and conditions for quenching, possibly in conjunction with energy recovery. In addition, there is a need for appropriate materials for the electrodes and material containment. Finally, many industrially successful systems may have to be part of larger industrial complexes in order to obtain optimum materials and energy utilization. The conceptual study of these systems would also be desirable.

Chapter 2

INTRODUCTION TO PLASMA PROCESSING OF MATERIALS

Plasma processing makes use of the plasma state, which is frequently referred to as the fourth state of matter, since more than 99 percent of the universe known to man is in the plasma state. The high energy content of a plasma compared to that of solids, liquids, or ordinary gases lends itself to a number of intriguing applications.

In general, a plasma consists of a mixture of electrons, ions, and neutral species. Although there are free electric charges in a plasma, negative and positive charges compensate each other, i.e., overall, a plasma is electrically neutral, a property known as quasi-neutrality. In contrast to an ordinary gas, the free electric charges in a plasma give rise to high electrical conductivities that may even surpass those of metals.

Plasmas may be generated by passing an electric current through a gas. Since gases at room temperature are excellent insulators, a sufficient number of charge carriers must be generated to make the gas electrically conducting. This process is known as electrical breakdown, and there are a number of ways in which this may be accomplished. The breakdown of the originally nonconducting gas establishes a conducting path between a pair of electrodes. The passage of an electrical current through the electrode gap leads to an array of phenomena known as gaseous discharges. Such gaseous discharges are the most common but not the only means for producing plasmas. For certain applications, plasmas are produced by electrodeless rf discharges, by shock waves, or by laser or high-energy particle beams. Finally, plasmas may also be produced by heating gases (vapors) in a high-temperature furnace. Because of inherent temperature limitations, this method is restricted to metal vapors with low ionization potentials.

For the following considerations plasmas produced by electrical discharge will be emphasized. In principle, such plasmas are divided into two types. The first is the "hot" or "equilibrium" plasma, which is characterized by an

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approximate equality between heavy particle and electron temperatures, i.e., the thermodynamic state of the plasma approaches equilibrium or, more precisely, local thermodynamic equilibrium (LTE). Such plasmas are known as thermal plasmas. LTE comprises not only kinetic equilibrium $(T_e = T_h)$ where T_e = electron temperature, and T_h = heavy particle temperature but also chemical equilibrium; i.e., particle concentrations in a LTE plasma are only a function of the temperature. Typical examples of thermal plasmas are those produced in high-intensity arcs and plasma torches or in rf high pressure, high-power-density discharges [1-3].

The second type of plasma is known as the "cold" or "nonequilibrium" plasma. In contrast to thermal plasmas, cold plasmas are characterized by high electron temperatures and rather low "sensible" temperatures of the heavy particles $(T_e >> T_h)$. Plasmas produced in various types of glow discharges, in low pressure rf discharges, and in corona discharges are typical examples of such nonequilibrium plasmas.

Thermal as well as nonequilibrium plasmas cover a wide range of temperatures and electron densities. Figure 2-1 shows the approximate range of electron temperatures and electron densities of natural and man-made plasmas. The electron temperatures are given in units of electron volts (1 eV corresponds to an electron temperature of approximately 7,740 K).
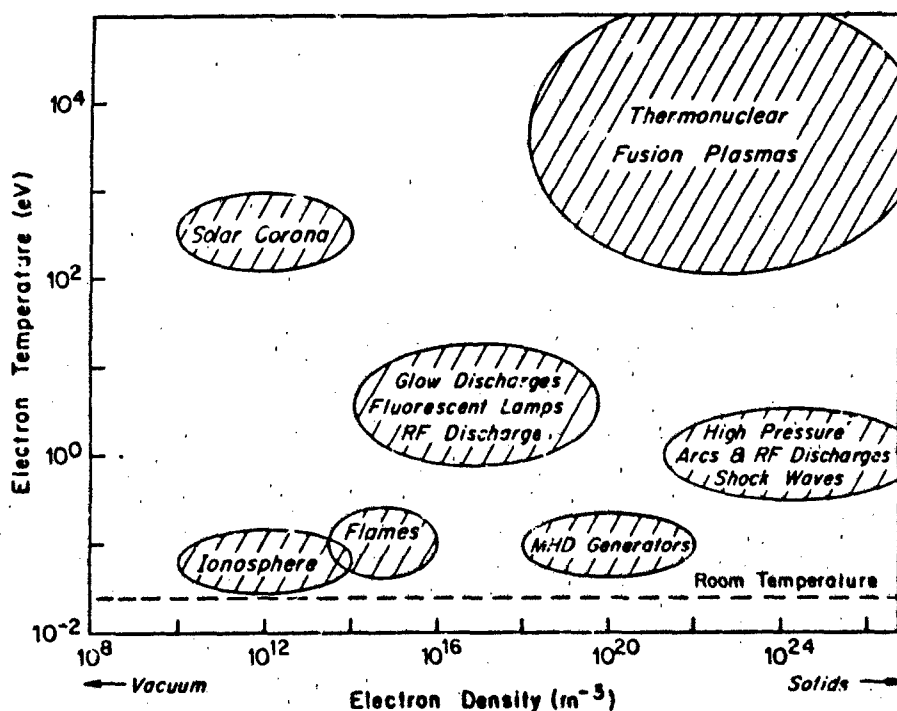
FIGURE 2-1 Classification of plasmas.

As a general criterion for the existence of a hot or a cold plasma, the ratio of E/p or E/n has been proposed (Σ = electrical field strength, p = pressure, n = particle number density). This criterion reflects the energy exchange process between electrons and heavy particles in a plasma. The collisional "coupling" and the associated energy exchange between electrons and heavy particles is enhanced by high particle densities or high pressures. High electric fields tend to increase the excess energy of the electron gas, therefore, thermal plasmas are characterized by small values of E/p or E/n. For cold plasmas, values of these parameters are higher, usually by several orders of magnitude. Figure 2-2 shows the separation of electron and heavy particle temperatures in an electric arc as a function of the pressure (100 kPa ≈ 1 atm).

Both thermal and cold plasmas have been known for many years, and there is a wealth of information available about them in the literature [4-13]. The commercially successful application of plasmas for materials processing, however, is relatively new, although a great deal of work has been done in this field. The unavailability of the required hardware, including diagnostic tools, as well as the lack of basic understanding of the interactions between plasma and materials, are the main reasons earlier attempts had little or no success. Over the past 25 years sophisticated hardware has been developed, and at the same time plasma diagnostics developed into a mature science which removes the major obstacles for the commercialization of plasmas as materials processing tools. In this context, advances in computer technology will continue to be crucial for the analysis and modeling of plasma and material interactions and chemical reactions under plasma conditions. In spite of these encouraging developments, plasma processing still suffers from a profound lack of fundamental knowledge. This will become increasingly clear in the following chapters of this report.
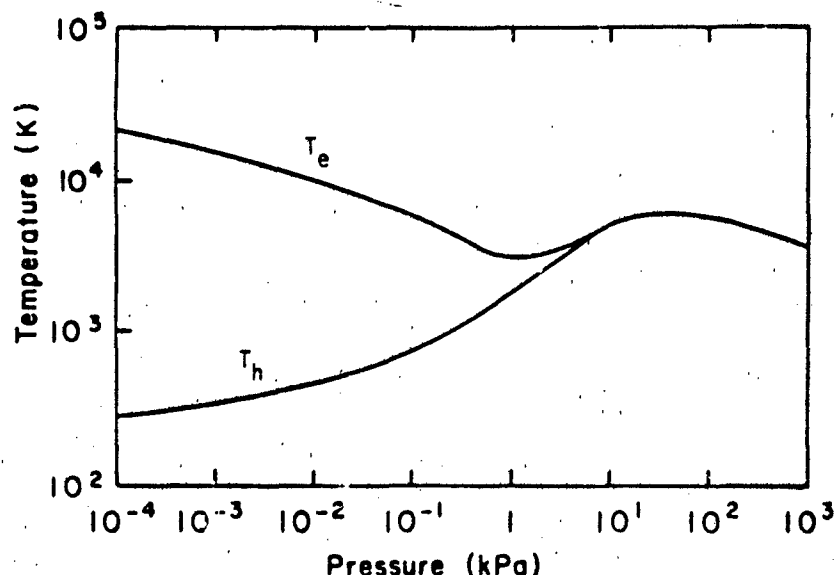
FIGURE 2-2   Behavior of electron temperature (T_e) and heavy particle temperature (T_h) in an arc plasma [2].

Industrial advances in the field of plasma processing have been hampered by the previously mentioned gaps in understanding of particulate matter interaction with plasmas. Although the knowledge generated in recent years fills some of these gaps, much more work needs to be done to establish a solid engineering base for industrial development.

In contrast to the development of more conventional technologies, this field cannot succeed without extensive interdisciplinary interactions. Knowledge in plasma physics, gaseous electronics, fluid dynamics, and heat transfer must be combined with experience in surface chemistry, electrochemistry, and materials science. Because of the high cost of equipment, especially for diagnostic purposes, the very nature of plasma processing makes the establishment of viable research groups rather difficult, especially in academic environments. Therefore it is not surprising to find so few university research groups in this field, and as a consequence the generation of basic knowledge in plasma processing of materials has been rather slow.

For the following discussion of the state of the art in this area, it is useful to consider the range of plasma parameters, indicated in Figure 2-3, that apply for thermal and for nonequilibrium plasma processing of materials.
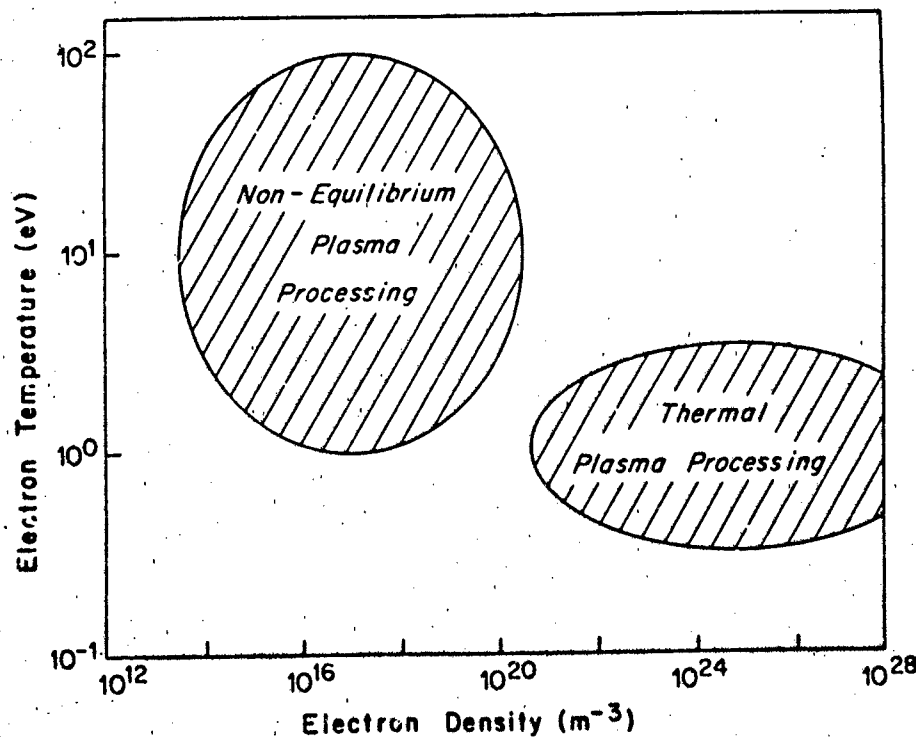
FIGURE 2-3   Plasma parameters for thermal and nonequilibrium plasma processing of materials.

Over the past decade, the availability of high-speed computers has
provided a strong incentive for modeling work in thermal plasma technology.
This approach, however, is not without problems due to the multi-component
mixture of gases and vapors that a plasma, in general, represents. Moreover,
modeling is restricted to relatively simple configurations (usually
two-dimensional) that may substantially differ from actual situations.
Although our level of basic understanding of thermodynamic properties and
transport phenomena in plasma systems has improved considerably over the past
years, the multi-component nature of actual plasma systems and the complexity
of the geometry impose severe limitations on the validity of modeling work.
Nevertheless, even simplified models are useful for understanding basic trends
and for determining the parameters that govern the behavior of plasma
systems. In addition, the results of such modeling work provide useful
guidelines for pertinent experiments.

As an illustration of recent results, Figure 2-4 shows a comparison
between measured and predicted isotherms in a free-burning, high-intensity
arc [14], and Figure 2-5 shows measured and predicted axial temperature
variations in a nitrogen/hydrogen plasma jet [15]. Although severe problems

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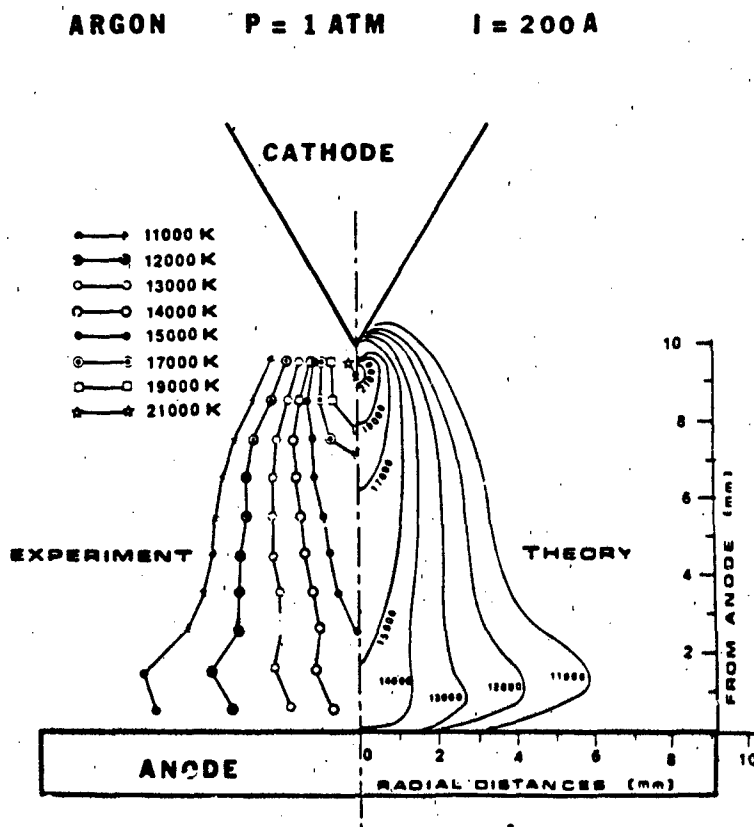
FIGURE 2-4   Isotherms of a free-burning, high-intensity arc [14].
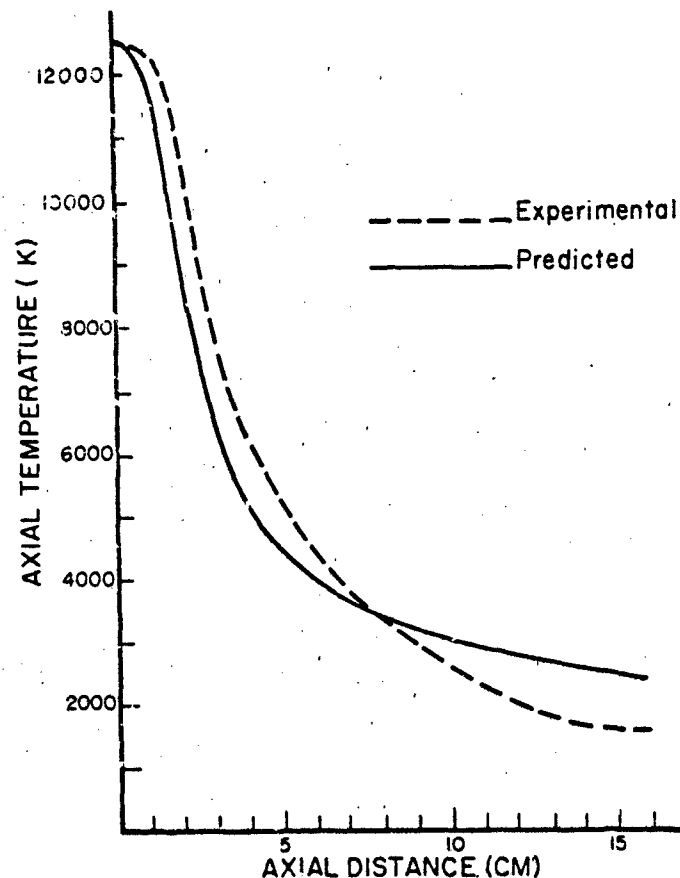
FIGURE 2-5   Axial temperature variation in a nitrogen/hydrogen atmospheric
              pressure plasmas jet [15].

have been experienced in the modeling of these systems, the results have
indicated reasonable agreement between predictions and measurements.

A number of laboratories in the United States and abroad have been
involved in modeling work associated with the interaction of particulate
matter with thermal plasmas. The results of this work, which are discussed in
the following chapters, are of considerable importance both for plasma
processing of materials and for plasma spraying.

Despite substantial improvements in our overall understanding of thermal
plasma behavior, a number of problems require intensive studies. In
particular, efforts are necessary to gain a better understanding of deviations
from LTE in the vicinity of electrodes and confining walls. In addition,
there is still a poor understanding of the motion and heating of particles in
rarified plasmas and in regimes of extremely steep temperature gradients.

Thermal plasma processing comprises melting and remelting technologies, plasma metallurgy, including extractive metallurgy, plasma deposition and rapid solidification techniques, plasma synthesis and consolidation, and other industrial applications that make direct or indirect use of thermal plasmas. With a few notable exceptions, thermal plasma processing is still in the laboratory or pilot-plant stage. The potential of many thermal plasma processes, however, is increasingly recognized, and there seems to be consensus among the experts that new emerging technologies in thermal plasma processing will have a strong impact on the economy.

Plasma metallurgy has a long and successful history. Arc welding, cutting, and spraying, arc melting of scrap, and plasma refining and alloying have been used commercially for many years. The key advantages of thermal plasma techniques as specifically applied to melting technology include (a) the ability to achieve a steady-state, uniform flow of partially ionized gas with bulk gas temperatures well above those obtainable with chemical (combustion) flames or resistance heater systems; (b) operation in an inert or reactive environment thus providing complete control of the atmosphere; and (c) a compact system that can process material in a variety of forms at high throughput rates and with relatively high electrical and thermal efficiency.

With only a few exceptions, thermal plasma melting technology in the United States is still in the laboratory or pilot-plant stage in comparison to foreign countries, where a variety of full-scale production systems operating at steady-state process power levels up to about 20 MW are in continuous operation. Thermal plasma melting and materials processing is an interdisciplinary technology in transition. New prospects for large-scale implementation of plasma melting technology by the domestic mining, metallurgical, iron and steel, specialty metals, and chemical industries appear most promising, based on some of the recent state-of-the-art advances.

There has been considerable interest in extractive metallurgy, as evidenced by numerous laboratory and pilot-plant-scale studies reported in the literature (extraction of iron, titanium, molybdenum, and ferroalloys). Recent developments include a plant being built in Sweden (SKF Steel Engineering AB) for recovering metals from various waste oxides and a sponge-iron plant under construction by South Africa's Union Steel Company. With the exception of the Swedish Plasmared process, however, there are as yet no commercial installations in operation.

Although plasma spraying is already a well-established commercial process, its science base is still in the developmental stage. Plasma spraying is considered to be one of the prime candidates for producing high-temperature-resistant coatings for turbine blades and anti-wear and anti-corrosion coatings, especially for high-temperature applications.

Recent developments in the field of arc plasma spraying, in particular the introduction of the low-pressure plasma deposition (LPPD) process, or vacuum plasma spray (VPS), have resulted in a renewed interest in the capabilities of plasma spraying. In conventional plasma spraying the deposition is carried out at atmospheric pressure, whereas in LPPD, the process is carried out in a

low-pressure environment. In contrast to conventional plasma spraying, LPPD provides major benefits, such as higher particulate velocities, which create greater than 98 percent dense deposits; broad spray patterns, which produce large deposit areas; and transferred arc heating of the substrate, which improves the deposit density and adhesion of the coating. These characteristics provide LPPD with the potential of becoming a viable method of consolidating powders for high-performance applications. Moreover, the LPPD process can be automatically regulated to make controlled deposits on complex geometries at reasonably high deposition rates (up to 50 kilograms per hour). Although this process is already widely used, its science base needs to be developed.

Thermal plasma synthesis is still in its infancy, despite great strides over the past years, not only in the United States, but also in Europe, in Japan, and in the Soviet Union. Fortunately, hardware development is in a more advanced state. Due to spin-offs from aerospace programs in the 1960's, a wide variety of ac and dc arc gas heaters as well as rf thermal plasma generators are available at present [2].

Two new developments that can be associated with plasma processing are:

1.   New materials and improved processing routes for conventional
      materials; new materials with unusual properties may replace or even
      surpass conventional materials that arc already in or expected to be
      in short supply.

2.   Rapid solidification leading in extreme cases to amorphous metallic
      alloys; the high temperatures and the associated extremely high
      heating and quench rates feasible in thermal plasma reactors offer
      interesting opportunities for such processes.

Rapidly quenched atomized powders coupled with traditional powder metallurgy processing have resulted in components having good high-temperature performance; in addition, the capability of generating near-net-shape components helps conserve the use of scarce raw materials. These powders can then be hot-extruded, hot closed-die forged, hot isostatically pressed, or liquid-phase sintered into a near net-shape that requires minimal machining, thus conserving materials.

Because of this potential, there is a strong incentive to produce fine metal powders and powders of metal compounds (nitrides, carbides, oxides) in thermal plasmas. A number of research laboratories are actively engaged in this work, and it is anticipated that it may take another 5 to 10 years before economically viable plant operation may be accomplished.

Significant progress has been made in the past few years in th t of applying nonequilibrium (cold) plasmas to the processing of materia , and surfaces. Depending on the particular application, both noble gas and molecular gas plasmas are employed in this processing. However, while the noble gas applications are relatively well understood phenomenologically, those requiring the use of molecular gases are not. This is due to the fact

that these gases generally involve various complex chemical reactions. Accordingly, the processing of materials and surfaces via the use of molecular gases has been and is presently based largely on an empirical or trial and error methodology.

In many applications employing noble gases, the plasma serves mainly as a source of energetic ions that transfer energy from the plasma to a solid surface by direct impact. Ion impact can produce atom displacement, rearrangement of molecular configurations, and sputtering. Sputtering is the basis for sputter etching and sputter deposition, techniques widely employed in the production of microelectronic and optical components, as well as for cleaning and coating of surfaces. Sputter deposition is used to produce thin films for a variety of applications, ranging from silicon integrated circuits, optoelectronics, and magnetic recording media to surface protection against corrosion and wear. The sale of sputtering equipment to this fast-growing industry alone is expected to be a $300 million per year business by 1985.

Molecular gas plasmas can produce highly reactive radicals resulting from electron-impact dissociation of parent molecules. Reactions between generated radicals can result in the deposition of thin films on substrates, a process which is known as plasma enhanced chemical vapor deposition (CVD). Reactions of radicals with substrates can produce surface alterations such as molecular rearrangement, surface cleaning, surface hardening, etching, and nonvolatile compound formation.

Deposition of both organic and inorganic films is possible. Some applications are photovoltaics, microelectronics, surface protection, polymer membrane formation, and textiles. Illustrative examples include the following:

- Amorphous silicon films containing large quantities of hydrogen, which show promise as cost-effective photovoltaics for solar energy conversion. (This material has immense potential for the manufacture of inexpensive photovoltaic devices--e.g., solar cells--and could lead to a very large industry; apparently numerous Japanese companies have development projects in this area.)

- Oxides and nitrides of silicon for use as dielectrics in silicon integrated circuits and other micro-electronic devices

- Polymer membranes for gas separation, water purification and biomedical applications

- Thin plasma polymerized films from fluoride and silicon compounds for waterproofing textiles

Surface alteration by reaction with plasma-generated radicals is the basis of a growing number of important applications. Relevant reactions are often strongly influenced by simultaneous impact of the surface by ions, electrons, or photons from the plasma. While this frequently produces desirable synergistic effects, such as enhanced reaction rates, it adds to the overall process complexity and thus makes detailed understanding and characterization more difficult.

Some key applications that demonstrate the diversity and usefulness of this facet of nonequilibrium plasma technology are the treatment of polymer surfaces to promote grafting, improve adhesive characteristics, or alter wettability, and plasma-assisted etching (dry etching) in the fabrication of silicon integrated circuits.

The latter application has become an indispensable part of very-large-scale integrated circuit (VLSIC) fabrication because of the unique capability to etch high-resolution, high-aspect-ratio patterns with micron-size dimensions. Dry etching ranks at or very near the top of the list of strategically important applications for nonequilibrium plasmas, since progress in VLSIC technology will be tightly coupled to progress in the development of dry-etching processes.

We expect the number of applications and the use of cold plasmas to increase rapidly during the next 10 years. There are many functions that can be accomplished in a cold plasma environment that would be difficult to accomplish in other situations. It is our opinion that a sustained research effort directed toward understanding the basic physics and chemistry in plasma-assisted etching and plasma-enhanced CVD would allow much more rapid progress in these fields. In particular, a large effort is required to develop diagnostics.

As previously mentioned, there is a wealth of information available in the literature on thermal and nonthermal plasmas. A selected number of pertinent references has been already cited [1-13], including those concerned with plasma diagnostics.

Journals that contain papers on plasma processing of materials include Plasma Chemistry and Plasma Processing, Journal of Applied Physics, Journal of Physics D: Applied Physics, AIChE Journal, Pure and Applied Chemistry, Journal of Physical Chemistry, Journal of Chemical Physics, Journal of Polymer Science, Journal of Electrochemical Society, Journal of Vacuum Science and Technology, Thin Solid Films, Journal of Material Science, Material Science and Engineering, High Temperature, IEEE Transactions on Plasma Science, International Journal of Heat and Mass Transfer, and Heat Transfer Journal. In addition, there are many foreign journals concerned with this subject. Because of translation problems, the large amoung of literature from the Sovie Union has not been covered in this report.

An extensive bibliography on Plasma Chemistry and Plasma Processing is available. It has been compiled and edited by A. T. Bell and H. Suhr through the subcommittee on Plasma Chemistry (IUPAC). The main volume contains more than 5000 references up to 1971, Supplement I has approximately 1400 references from 1971 to 1975, and Supplement II has approximately 1800 references from 1975 to 1979. (For further information contact Professor H. Suhr, Institut fuer organische Chemie, Auf der Morgenstelle 18, 7400 Tubingen, Federal Republic of Germany.)

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For the rapid dispersion of research results there are two major conferences: the International Symposium on Plasma Chemistry and the Gordon Conference on Plasma Chemistry.

In addition, various other conferences (MRS, ASME Gas Turbine Div., AVS, etc.) increasingly include special sessions on plasma processing of materials.

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Chapter 3

THERMAL PLASMA MELTING AND REMELTING TECHNOLOGY

As with many other fields of science, thermal plasma melting and processing technology has experienced some severe oscillations in direction and emphasis over the past 15 years. The recent energy crisis has resulted in renewed emphasis on plasma technology. Long-range projections on coal and nuclear fuel availability suggest that an "electric energy economy" may be part of the solution to the long-term energy problem. As the United States and foreign countries shift more toward electricity as the major energy base, numerous high-temperature plasma material processing applications will inevitably result.

In some cases, merely a retrofit of an existing process will take place. In others, an updated processing system will replace an obsolete system for generating the same final product at reduced cost and increased efficiency. Finally, completely new processing systems will be initiated in the future to provide new materials and products not defined at this time.

The key advantage of thermal plasma techniques as specifically applied to melting technology include (1) the ability to achieve a steady-state, uniform flow of partially ionized gas with bulk gas temperatures well above those obtainable with chemical (combustion) flames or resistance heater systems, (2) operation in an inert or reactive environment, thus providing complete control of the atmosphere, and (3) a compact system that can process material in a variety of forms at high throughput rates and with relatively high electrical and/or thermal efficiency.

Over the past several years, researchers in the field have pioneered the design of several novel plasma systems that meet the stringent requirements of full-scale industrial applications (including high throughput, reliability, efficient utilization, and a good return on investment). Much of the material presented in this chapter has been distilled from the literature, but a significant input has been derived from plant visits throughout the world and from personal discussions; the information presented here could only have been gathered by such interactions.

FUNDAMENTALS OF PLASMA MELTING TECHNOLOGY

Plasma as a Heat Source

As noted in the intr ductory chapter, the word __plasma__ will refer to that gaseous region of an ele tric discharge that is characterized by intense luminosity occurring sin ltaneously with the presence of electrons, atoms, and positive and negative ions. In this state the gas, which normally is nonconductive, will be in a partially ionized state and therefore will display a significant electrical conductivity. This state of matter can be produced through the action of either very high temperatures or high electric fields. In such a plasma discharge, the free electrons gain energy from the applied electric field and subsequently lose this energy through collisions or recombination with neutral gas particles. This process, depending on the gas composition, can also lead to a variety of new species such as free atoms, ions, free radicals, and metastable particles. Table 3-1 shows typical operating regimes that distinguish the thermal plasma and radio frequency (rf) discharges from glow-type discharges.

TABLE 3-1   Typical Operating Regimes of Discharges

Discharge Type	Frequency	Power, Q	Pressure, P	Flow rate, M	Gas temp, Tg
Glow	--	<5 kW	≤ 100 torr	$\leq$ mg/s	< 100 K
RF	1 kHz -- $\leq$40 MHz	1 kW -- 1 MW	10 torr --1 atm	<50 g/s	1000 -- 10,000 K
Arcs	--	1 kW -- 10 MW	100 torr --40 atm	< 500 g/s	3000 -- 30,000 K

Figure 3-1 illustrates several features that distinguish a thermal plasma arc from other type discharges. In general, the voltage required to sustain an arc discharge is much lower than for other types of discharges. Furthermore, the potential distribution changes rapidly near the electrodes in the areas referred to as cathode and anode fall regions. The cathode fall assumes values of about 10 volts relative to values greater than 100 volts in glow discharges. The relatively low electrode fall voltages are attributed to the efficient electron emission mechanisms at the cathode. Depending on the energy balance of the arc column and its length, the total voltage drop may be relatively high. The specific voltage gradient also depends on the pressure, monatomic or diatomic gas type, metal or liquid vapor environment, etc. For example, a plasma arc column operating in air at atmospheric pressure will have a column voltage gradient in the order of 10V/cm. If external aerodynamic or magnetic field stabilization is applied to the column along with higher-pressure operation, total arc voltages exceeding 9,000 volts can be reached together with very high column voltage gradients. Another feature of thermal plasmas operating at high-pressures, ~1 atm, is that a significant fraction of the total plasma power is dissipated as radiation (normally in the range of 15 to 45 percent).
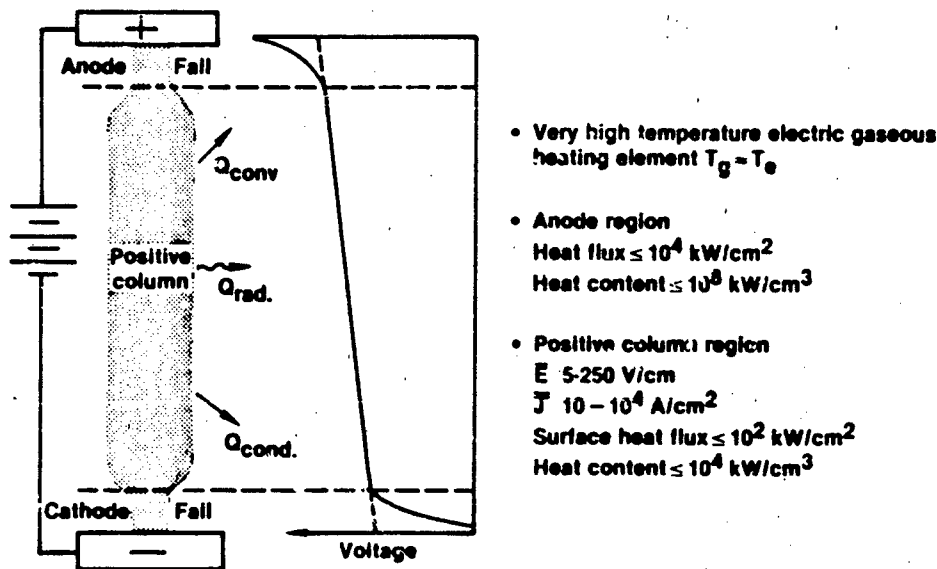
FIGURE 3-1 Thermal plasma arc characteristics.

Depending on the particular application and required performance, different electrode materials are used. In the few cases where electrode contamination is permitted, graphite or carbon electrodes are used. Most applications require minimum contamination. In the use of nonconsumable electrodes, long lifetime is a prerequisite that must be provided by minimizing electrode erosion. The penalty paid in this case is a reduction in the overall thermal efficiency. Another technique for reducing electrode erosion is using external magnetic and/or aerodynamic fields to rapidly rotate or move the arc attachment points on the electrode surface, thus effectively spreading out the heat load. Depending on the application, either cold or hot-type cathodes are used. Cold cathodes rely primarily on field emission as a source of electrons, compared to the thermionic emission provided by the hot type. The geometry and shape of the cathode is an area that has received considerable investigation and depends strongly on the selected current operating range. Pin-type cathodes (typically 1-cm-diameter with either a conical or rounded shape) are normally used for steady-state operation in the 10^3 A range. A transition to a button-type geometry is required when current levels exceed about 10^3 A. For current levels higher than about 4 x 10^3 A, a hollow cathode geometry is introduced to provide a larger electrode surface area for enhanced electron emission distribution. Electrode erosion and associated contamination is a subject that has plagued researchers for many years. This situation becomes more aggravated if oxygen, air, or other reactive gas mixtures are used in the plasma reactor. Inert gas shielding (e.g., argon shroud) is one technique that has been successfully developed to solve this problem

The most widely used cathode material is tungsten. Thoriated tungsten or barium-calcium-aluminate or lanthanum-doped tungsten are also used; the doping is added to lower the work function. The work function is a measure of the work in volts necessary to remove a unit charge of electrons from the surface. In some designs, a hot cathode is concentrically located within a highly cooled copper well or is cooled by a high-velocity inlet gas flow. The gas flow technique, if properly applied, also aids in maintaining the discharge attachment at the central location of the cathode which improves stability and provides a rotationally symmetric geometry. Hot cathodes are limited to the low to moderate-pressure regime. In cold cathode designs, copper alloys, including sintered copper-tungsten, have been used.

The anode, in contrast to the cathode, is subjected to very high fluxes and consumes a large percentage of the total power in the plasma arc. Consequently, efficient cooling schemes (water or gas transpiration) are required if the plasma arc reactor is used as a gas heater; when used in a melting or remelting application, the work piece or material to be melted normally becomes the anode. In some cases, depending on source configuration, the polarity is reversed, with the material to be processed becoming the cathode. In many of the plasma arc reactors used for melting, an isolated (electrically floating potential) nozzle assembly or "constrictor" is used to aid in the arc confinement and stabilization.

The choice of gas flow patterns (e.g., coaxial, vortex, or combinations thereof) near the electrodes and within the plasma arc reactor used for melting and processing materials is important for providing good stability and improved lifetime. The coaxial flow scheme is the most popular, but sometimes a tangential component (i.e., vortex flow) is also superimposed, particularly in the high-current-level operating regime.

Basic Types of Plasma Reactors

Different types of plasma arc reactors are currently in use for materials processing. These include dc, ac, and rf as the primary power input (see Table 3-2). The most prevalent type is the constricted dc plasma arc reactor. Figure 3-2(a) is a simplified sketch of a typical thermal plasma torch configured in the nontransferred mode. In this mode, an arc is established between an axial water-cooled pin-type tungsten cathode and an annular water-cooled copper anode. In this configuration, a coaxial, vortex, or combined coaxial-vortex gas stream is introduced into the chamber; this flow moves the anode attachment into the constricted region and also provides stabilization. This lengthens the arc, raises the voltage, and results in higher temperatures because of constriction. Centerline temperatures can range between 8,000 and 30,000 K with corresponding high radial temperature gradients. Typical power levels for plasma torches of this type are 75 kW; the associated thermal efficiencies normally range between 55 and 85 percent. One or more power supplies may be used to provide superimposed sources. In general, the nontransferred mode is limited in lifetime due to erosion of the nozzle, especially at high currents. Use of a vortex-stabilizing flow can aid in extending the lifetime in the nontransferred mode of operation. Typical electrode lifetime with vortex augmentation is approximately 80 hours. With proper design and choice of operating parameters, contamination levels in the plasma positive column can be held to about 5 ppm, which is an acceptable level for most applications.

TABLE 3-2 Types of Thermal Plasmas

- Direct Current
  Plasma reactor/torch
  - Nontransferred/transferred mode
  - Wall/gas/magnetic stabilized
  - Pin/hollow electrodes
  - Fixed/movable electrodes
  - External magnetic field augmentation

- Alternating Current
  Plasma furnace
  - Single and multi-phase
  - Fixed/movable electrodes
  - External magnetic field augmentation

- Radio frequency
  Electrodeless reactor
  - Inductive coupling
  - Capacitive coupling

Considerable development has occurred over the last 10 years in the design and optimization of plasma sources (specifically dc torches) operating in the nontransferred mode for specific refractory material spraying, welding, and cutting operations. The electrode and nozzle size and shape, gas mass flow rates, gas mixtures, and associated flow patterns are all key parameters for optimizing a source for each particular application. Within the last 5 years there has been about a threefold increase in the number of companies that market and use plasma torches of this type. However, they are relatively expensive; therefore, many users custom-build their own units according to their particular specifications.

For applications where more power is required to be coupled into the work piece (or metal to be melted), the transferred mode of operation is used, as shown in Figure 3-2(b). In this case, the work piece normally becomes the anode, whereas in the nontransferred mode shown in Figure 3-2(a), the nozzle of the arc torch becomes the anode. The transferred mode configuration permits much longer plasma arcs, with higher currents achievable at significantly higher voltages. This results in more power into the plasma for the same current as the nontransferred mode and a more efficient power deposition into the materials, since the anode attachment and corresponding heat flux is on the surface of the work piece instead of the anode nozzle with its associated thermal losses. For applications such as heating and melting, the transferred mode is more efficient than the plasma torch nontransferred mode. The plasma discharge is also more stable in dc operation, compared to pulsed dc or ac. The arc column does not have to cycle through zero current, with the associated instabilities and significantly higher open-circuit voltage requirements. The majority of all plasma reactors currently being used for melting and remelting operations operate in the transferred mode; therefore, this review will emphasize that type.

a) Plasma arc jet (torch), non-transferred mode

b) Plasma arc, transferred mode
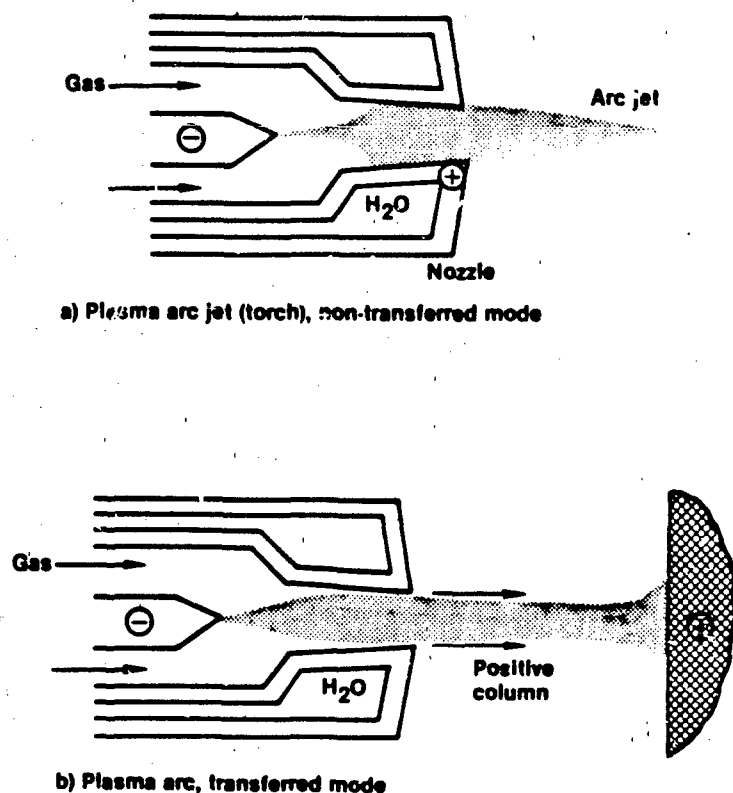
FIGURE 3-2 Examples of dc thermal plasmas: (a) plasma arc jet (torch), nontransferred mode; (b) plasma arc transferred mode.

One of the problems associated with the transferred mode of operation is ignition. Normally this is accomplished by first starting a pilot discharge, using a high-frequency starter system between cathode and nozzle and then transferring the main discharge to the work piece. Another technique is to use an auxiliary starting bar that is inserted between cathode and work piece and then withdrawn upon discharge ignition.

The ac types of plasma arc reactors make up a separate category (normally for gas heater applications). Some of the ac-type reactors operate in the 60-Hz regime. In this case, a high frequency ignition unit is used to re-establish the arc after each zero current point. By using water-cooled coaxial copper electrodes together with external magnetic field augmentation for arc attachment spot movement, a wide variety of gases can be heated with this type of device. Typical efficiencies are 60 percent. Figure 3-3 is an example of an ac type being developed and used in France. In this case, three movable electrodes arranged about the central axis with a coaxial sheath gas are employed. Initially the electrodes are brought together in the plasma jet from an auxiliary dc torch system; this is followed by 3-phase ac arc ignition. A major disadvantage of this type of system is the relatively high electrode material loss.

One deviation from the conventional plasma reactor is the so-called centrifugal furnace. Figure 3-3 illustrates this type reactor. The basic principle invokes centrifugal force to retain a stable layer on the wall after the material is melted because of interaction with the plasma jet(s). Attack of the furnace container is minimized by maintaining the required temperature gradient through the ceramic wall. Fusion of ceramics is the principal application of this type of reactor. Additional variations of this centrifug furnace may include using multiple plasma jets at each end of the furnace and transferring a long, high-voltage, high-power dc or ac discharge between them. When a tilt mechanism is incorporated, the molten contents can be poured into molds or quickly quenched to yield powder.
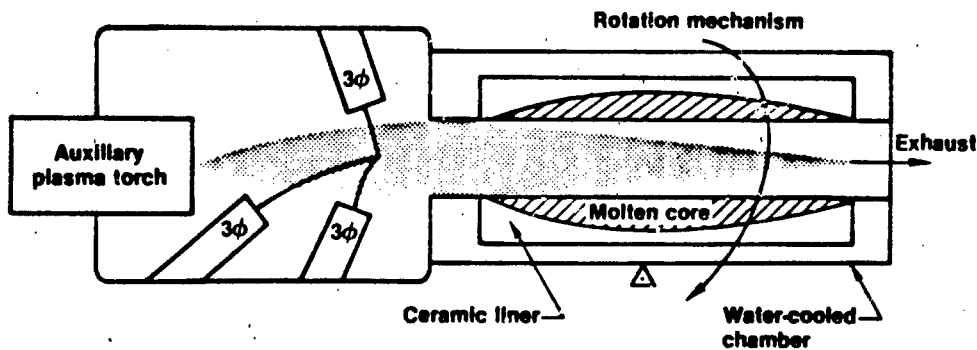
FIGURE 3-3 Example of ac thermal plasma (centrifugal) furnance.

All the thermal plasma reactors described use different forms of electrodes. Another class, primarily confined to laboratory scale, is the electrodeless radio frequency (rf) plasma. Figure 3-4 is a sketch of the basic configuration. In this type of reactor the electric power is coupled to the plasma via rf work coils (for typical operating ranges). In general, the rf plasma reactor is more expensive than other types, but it does possess the unique advantage of being able to heat all types of gases (including highly reactive and corrosive materials) to high temperatures with negligible contamination. A disadvantage of these devices is the magnetohydrodynamic problem of having a large fraction of the total gas feed not penetrating the main core of the plasma where the high-temperature reaction region exists.

In summary, from the standpoint of commercial applications, the highest thermal efficiency is required; thus the selection of the transferred mode of operation with a dc source is favored. When these dc type devices are properly designed to incorporate nonconsumable electrodes, relatively long lifetimes at high power levels are achievable with minimum contamination.
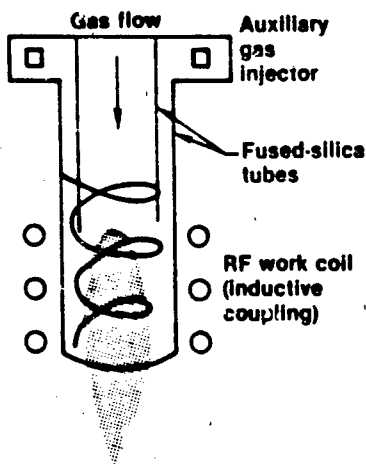
FIGURE 3-4 Example of rf thermal plasma torch.

Advantages

Several key advantages of employing thermal plasma reactors for melting and materials processing are listed in Table 3-3. Use of a thermal plasma type of heat source is characterized by a high concentration of energy and associated high gas temperatures. This results in both high throughput and melting rates. The flexibility afforded by operation under an inert environment minimizes contamination of the material to be melted or processed. Complete control of the atmosphere is also achievable. Operation at elevated pressures with an inert gas minimizes the loss of high-vapor-pressure constituents and also eliminates the need for expensive vacuum pumping equipment as required with vacuum arc remelt (VAR) and

TABLE 3-3 Major Advantages of Thermal Plasma Melting Techniques

● Steady-state uniform flow of very high temperature gas

● Complete control of atmosphere (inert or reactive)

● Minimum contamination and loss of volatile constituents

● Capability to process different forms of material

● Compact system with high throughput rates

● High thermal/electrical efficiency

electron beam (EB) melting systems. With this type of heat source, material melting rate and heat addition (superheat) to the molten pool are independent of the electrode feed rate, as compared to VAR systems. By employing nonconsumable electrodes, negligible contamination is achievable. Remelting under a reactive gas environment permits insitu chemical treatment. Use of dc plasma reactors results in considerably reduced voltage fluctuation compared to competing systems. The option also exists for refining operations using slags and direct alloying, as in the case of nitrogen injection. Other features include the ability to achieve dense ingots during primary melting that are free of shrinkage voids; in addition, the surface finish is good.

Features of the plasma arc type of remelting system compared with other remelting processes are listed in Tables 3-4 and 3-5.

TABLE 3-4 Comparison of Consumable Electrode Remelting Processes

Features	Vacuum arc remelt	Electroslag remelt
Atmosphere	Vacuum	Air, Ar, 1 atm
Power vs melt rate	Dependent	Dependent
Solidification control	Difficult	Difficult
Refining by slag	No	Yes
Degas (H, N)	Slight	No
Deoxidation	High	Moderate
Progressive solidification	Good	Good

TABLE 3-5 Comparison of Nonconsumable Electrode Remelting Processes

Features	Electron beam remelt	Plasma arc remelt
Atmosphere	High vacuum	Ar, H2, low/high P
Power vs melt rate	Independent	Independent
Solidification control	Possible	Yes
Refining by slag	No	Yes
Degas (H, N)	High	Slight
Deoxidation	High	High
Progressive solidification	Good	Very good

EXAMPLES OF PLASMA MELTING REACTORS

To date very few of the wide variety of plasma devices, including the
types described here, have been developed for production-scale operation.
This is especially true in the United States, where industries that could have
taken advantage of the plasma processing system have failed to do so. As of
1983, the United States is definitely behind foreign countries (specifically
the Soviet Union, German Democratic Republic, and Japan) in established
commercial-scale plasma processing reactor systems for melting of materials.
Those devices and associated processes that have achieved commercialization
are operated in a proprietary manner. Little or no information on the devices
and their operating characteristics is reported in the open literature. In
the following, a brief description is given of several selected examples of
these devices where information is available.

United States

Furnaces

One of the first thermal plasma reactors used to melt steel was the Linde
Corporation reactor (Figure 3-5), introduced almost 20 years ago [1]. The dc
plasma source was operated in the transferred mode under an inert argon
environment. The operating voltage was relatively low (less than 100 V); the
dc plasma source was mounted centrally within the top of the reactor. The
plasma arc operated in a stable mode that was due to a combination of low flow
rates and a relatively short plasma positive column (approximately 0.1 m).
The bottom electrode was water-cooled copper, electrically connected to the
molten pool of material to be processed. Over 100 hours of operation was
reported at current levels exceeding 10^3 A. Other features included a
magnetic coil connected in series with the discharge for stirring the molten
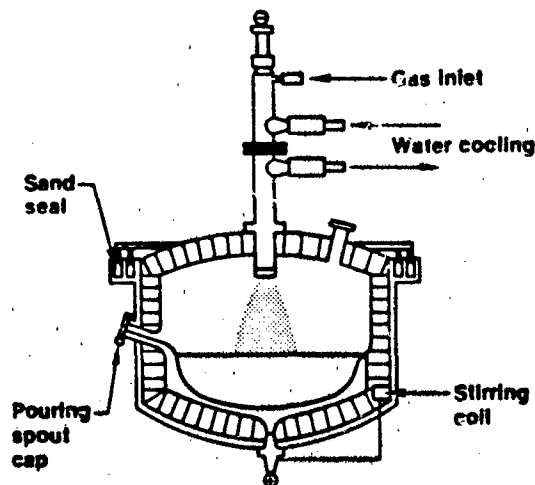
FIGURE 3-5 Schematic of Linde Plasmarc furnace.

pool. The Linde results, including scale-up from 1 to 1C tons, indicated that high-quality steel could be produced relative to that obtained by vacuum melting technology. Rapid wear of the bottom electrode, water leakage from the plasma source unit, and high erosion of the refractory lining caused by the abrasive action of the magnetically mixed molten material were identified as potential problem areas.

Bethlehem Steel Company was a pioneer in demonstrating the advantages of thermal plasma reactor processing for commercial-scale ore reduction. Bethlehem has a patent [2] for a falling-film plasma reactor that uses a high-power plasma arc (2,000 V, 500 A) to heat feedstock that melts down a vertically oriented hollow electrode. Being in the current-carrying path of the plasma, the liquid film is subjected to ohmic heating, along with convection and radiation heating. Figure 3-6 is a schematic of this type of furnace. The plasma arc is stabilized by a vortex gas flow between a tungsten cathode and a cylindrical water-cooled copper anode. Iron oxide fines are pneumatically transported to the anode section; the ore fines melt on contact with the hot plasma gas and form a falling liquid film in the hollow anode section. Metallurgical reduction processes are reported to take place within the falling film. The main advantage of the process is claimed to be the relatively long residence times obtainable, thus giving resultant high yields via improved heat transfer and direct contact of the oxide and reductant material required for the reaction. The falling-film residence time is controlled by varying the plasma gas feed rate, ore feed rate, plasma power level, and feedstock content. In addition, the film serves to thermally insulate the anode, since a solid layer is formed on the cooled surface of the anode, which helps in reducing electrode erosion.
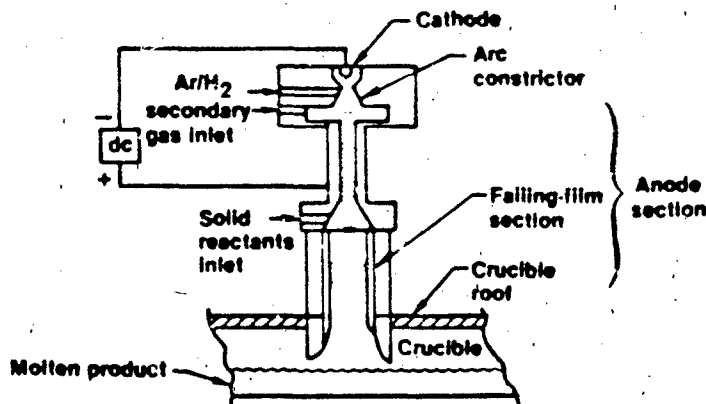
FIGURE 3-6 Bethlehem Steel Company falling-film reactor.

The falling-film plasma furnace was originally developed for iron oxide and later for vanadium oxide processing. The preliminary experiments on the direct plasma reduction of iron oxide were conducted at power levels of about

100 kW; favorable results led to a scale-up in power to the 1 MW range (2,000 V, 500 A). A mixture of methane and hydrogen was used for both the primary plasma gas and the reducing species. No slagging additions were necessary to maintain good flowability. In the large furnace the lowest specific energy consumption reported was about 2.6 kWh per kilogram of iron; this is approximately 15 percent greater than the theoretical specific energy requirement.

The specific power consumption decreases with smaller sizes of feedstock material, higher reactant/plasma gas ratios, higher throughput rates, and lower gas enthalpy. It should also be noted that at the reference lower specific energy consumption level, the electrical energy consumption of the falling-film dc plasma reactor is approximately equal to the total energy equivalent input of conventional steelmaking. Full-scale commercial steelmaking would require plasma reactors of about 500 MW. This represents a significant scaling above the 1 MW level and would probably require a configuration involving multiple plasma sources. Alternately, plasma arc steady-state currents exceeding 25,000 A would be necessary in large-scale source units; this is beyond the present state of the art. Therefore, based strictly on energy requirements, the plasma reactor technique does not excel over conventional steelmaking. This led to Bethlehem's discontinuing its effort in this area of direct iron ore reduction. One field that does look promising for this type of reactor is the so-called mini-steel-plant application.

Emphasis was then shifted to use of this type of falling-film plasma reactor for the reduction of vanadium ore concentrates into ferrovanadium and vanadium metal. To produce ferrovanadium, a variation of this type of reactor was developed at the 0.5 MW power level that operated at a higher enthalpy. This was dictated by the higher temperatures required in the production of ferrovanadium. Ferrovanadium (48 to 55 percent V), using coke fines as a reducing agent, was produced at a specific energy requirement of about 3.6 kWh per kilogram; this reactor was reported to demonstrate the commercial-scale production of 570 tons per year. With a further reduction in specific energy requirement projected for larger scale units, residence times of up to 2 minutes were achievable in the electrode region. However, it was not conclusively verified that a significant fraction of the conversion takes place in the falling film, compared to the molten melt/hot crucible region. As of now, Bethlehem Steel Company has limited development work in the ferrovanadium field. It reduced its activity in tool steel manufacturing about 3 years ago, primarily because ferrovanadium is readily and economically available on the open market.

Only a few other U.S. companies use thermal plasma reactors on a commercial scale. These are Associated Minerals Consolidated (AMC), formerly TAFA/IONARC, Plasma Materials Incorporated (PMI), and Plasma Energy Corporation (PEC). The AMC reactor is used in processing zircon via a carbon electrode scheme [3]. PMI employs a nitrogen dc plasma source to spheroidize particles of magnetic iron oxide used in photocopy machines with a magnetic brush developer system [4]. A sketch of the basic PEC plasma furnace is shown in Figure 3-7. This type of system is being used for scrap melting, electronic scrap processing, and cement production [5]. Typical power range of this transferred-arc-mode system is 150 to 300 kW.
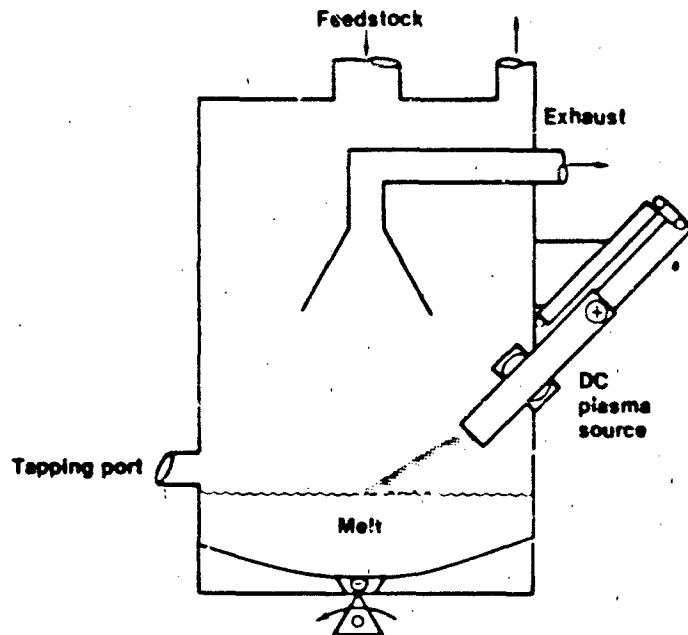
FIGURE 3-7 P.E.C. plasma furnace.

Agglomerators

The Frankel Company (Compton, California) is the only facility in the
United States that uses a thermal plasma reactor for agglomerating (i.e.,
partially melting) titanium scrap, virgin sponge, and master melt alloys into
porous bulk-weldable electrodes (approximately 5-ton ingots) that are used in
secondary VAR processing. Figure 3-8 is a sketch of the Frankel thermal
plasma agglomerating reactor [6]. The single dc plasma source (modified
Linde/Schlienger design) is vertically oriented within a large (2-m-diameter)
steel tank. Inside the tank is located a full-length track on which a mold
trolley traverses. The main components of this system are an approximately
1-MW dc thermal plasma source; a rectifier-type power supply; a charging
hopper/chamber system; a vacuum system; a closed-loop water cooling
system; an argon gas supply; and master control stations (one for material
control, one for plasma source control). The relatively low-voltage plasma
source (approximately 200 V) operates in the transferred mode on argon gas
with coaxial plus swirl flow for aerodynamic arc spot movement. The source
uses water-cooled copper for the electrode. With this type of design,
lifetimes of greater than 100 hours are achievable.

A unit of this size can process about 0.5 tons per hour. A batch-loading
procedure is used; therefore, for a complete ingot, the reactor must receive
multiple charges. After initial chamber pump-down to vacuum conditions, the
plasma melting operation takes place at slightly above 1 atm. At half maximum
power operation (500 kW), approximately 0.01 m^3/s of argon gas is consumed.
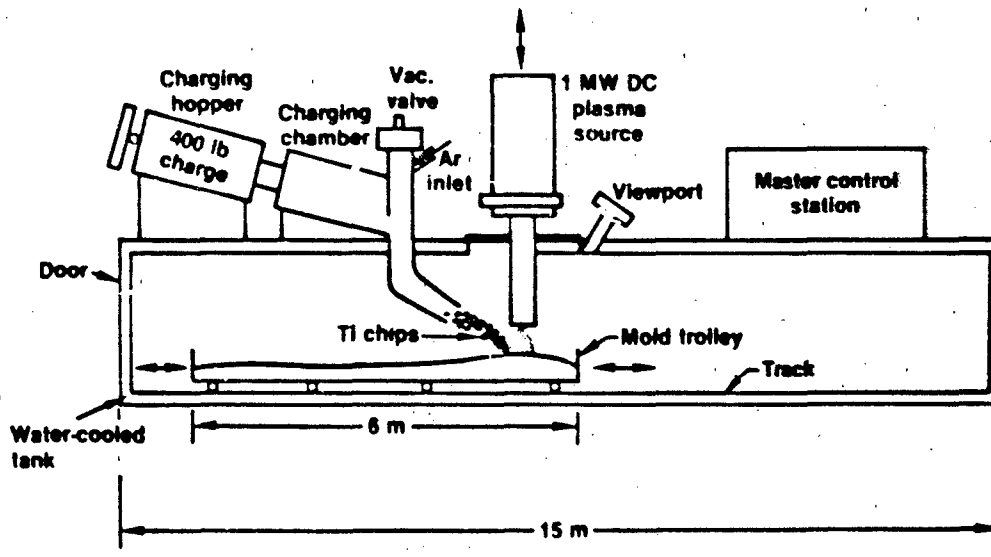
FIGURE 3-8   Schematic of Frankel plasma melt facility for titanium electrode
agglomeration and fabrication.

Before each melting operation, the mold trolley assembly (water-cooled
rectangular split halves) is preset for the diameter of the electrode desired
(typically 0.5 m). A 5-ton electrode requires a total of about 14 hours of
processing time. Following electrode fabrication, the material is shipped to
VAR melters for subsequent homogeneity and chemistry adjustment, according to
specifications and final product use.

Note that this type of plasma scrap alloy agglomeration process relies on
proper scrap treatment and classification prior to the actual melting step.
No provision is made for the removal of deleterious inclusions. No details
are available as to specific power requirements, overall system efficiency, or
utilization factors.

Foreign

Furnaces

A wide variety of reactor designs for the melting of metals have been
reported in the foreign literature over the past 10 years. The following
discussion highlights some of the features and status.

The central research laboratory of Daido Steel Company Ltd. (Nagoya,
Japan) has been very active over the past 10 years in developing plasma arc
remelting techniques applicable to steels, superalloys, and nonferrous

metals. Their initial R&D started with several 50 kW plasma arc furnaces and has steadily progressed up to the megawatt range for plasma progressive casting (PPC), plasma skull casting, and oxide reduction using a hollow cathode plasma furnace.

Recent emphasis has been placed on the plasma induction furnace (PIF) system [7]. This integrated thermal plasma technique provides both a protective inert argon atmosphere over the molten pool and the supplemental power required for keeping the thin layer of slag molten. A 0.5-ton and 2.0-ton unit are in operation; the former is a pilot-plant reactor for developmental work and the latter an industrial production facility. Figure 3-9 shows the basic reactor; it is a good example of the progress and status in melting technology that has occurred within a period of about 5 years. As a result, Daido's production rates have increased from 200 tons per year to 6,000 tons per year. A large fraction of the total increase in capacity has gone into copper and manganese alloys and the nickel-base alloys. Daido has recently made the transition to a 5 ton reactor. Table 3-6 compares the standard vacuum induction furnace (VIF) and the PIF system. The major advantages include the use of greater than 50 percent scrap; the capability of melting a wide range of alloys such as copper and manganese; a high level of cleanliness; low melting costs; and very high melting yield. High yields of all alloy additives have been obtained. The main disadvantage is the use of relatively high flow rates of argon gas. For reference, the Daido 2-ton PIF system operates at a total power of 1 MW (600 kW induction, 400 kW plasma) and employs an additional 200 kW for induction stirring. Nominal melting capacity is 220 tons per month; melting time is about 3 hours (additional 1 hour for refining), and the measured power consumption is 10^3 to 1.3×10^3 kWh/ton.
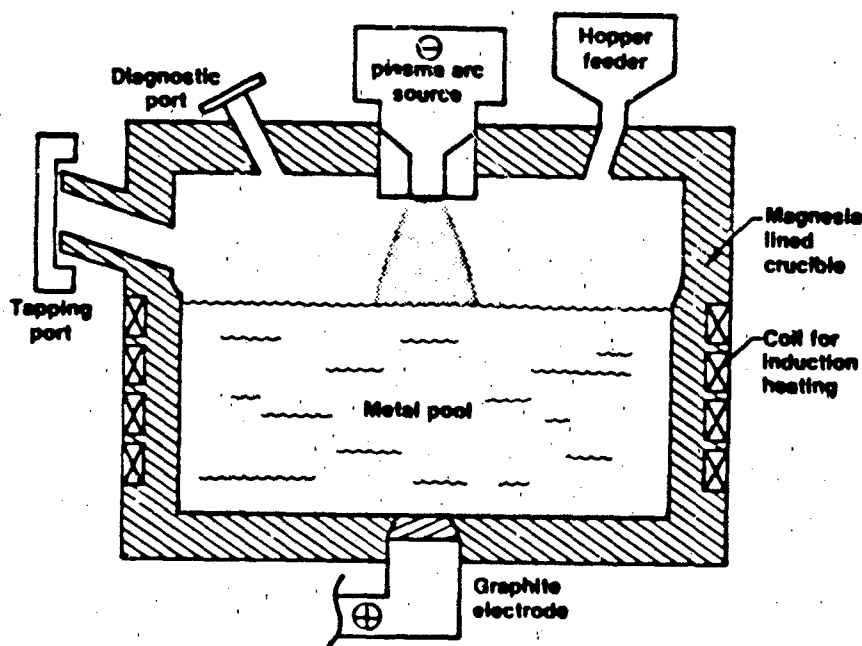
FIGURE 3-9 Daido Steel Company plasma induction furnace.

TABLE 3-6 Comparison of VIF and PIF Systems

Characteristic	VIF	PIF
Volatilization	High	Low
Mechanical property	Good	Good
Workability	Excellent	Good
Yield (melting) percent	98	98.9
Product yield (total)	75	85
Melting cost (index)	100	59
Oxygen	5-15 ppm	8-25 ppm
Nitrogen	10-30 ppm	10-50 ppm
Hydrogen	1 ppm	2-5 ppm
Desulfurization	10 percent	50-85 percent
Decarburization	90 percent	70 percent

Two areas receiving continued research and development at Daido are closed-loop recycling systems for the relatively expensive argon gas and new techniques for inducing molten pool stirring. One technique involves using different coil windings and a polarity shift; thus a dual vortex type of mixing pattern is obtained, with the molten material rising at the crucible boundary at one polarity and falling during the other. The slag thickness in this type of system is nominally about 10 cm.

When the PIF is used for high-chromium alloys, a hollow cathode configuration is employed. Comprised of a series of concentric tubes, the central bore transports the material to be processed via an oxygen carrier. Surrounding the inner nozzle is a hollow cathode assembly and two concentric annuli for argon injection. A water-cooled outer shroud surrounds the entire cathode. In general, the Daido PIF system has provided good slag refining capability and relatively high overall recovery of primary species and added alloys. The final product quality when processed via the PIF is about equivalent to the VIF in the majority of commercial applications.

Plasma primary melting reactors using a plurality of sources projecting through the sidewalls have been commercialized in the German Democratic Republic. The original reactors consisted of approximately 5-ton units with a single plasma source (transferred mode) located in the roof; maximum operating currents were 6,000 A using a tungsten alloy disc-shaped cathode. The alloying elements used are either lanthanum, thorium, or yttrium, which aid in reducing the thermionic work function. This permits sustained operation at the high currents and relatively low voltages (less than 500 V) by providing a relatively low arc cathode attachment temperature. Figure 3-10 is a schematic of a reference plasma melting reactor. Both 10-ton and 30-ton melting capacity units are in operation at the VEB Edelstahlwerks at Freital [9]. They are used in continuous operation for melting iron and nickel base alloys, stainless steels, and high alloy tool steels under an inert argon environment. The stainless steel melting is conducted both with and without nitrogen addition. The walls and roof are lined with bricks of
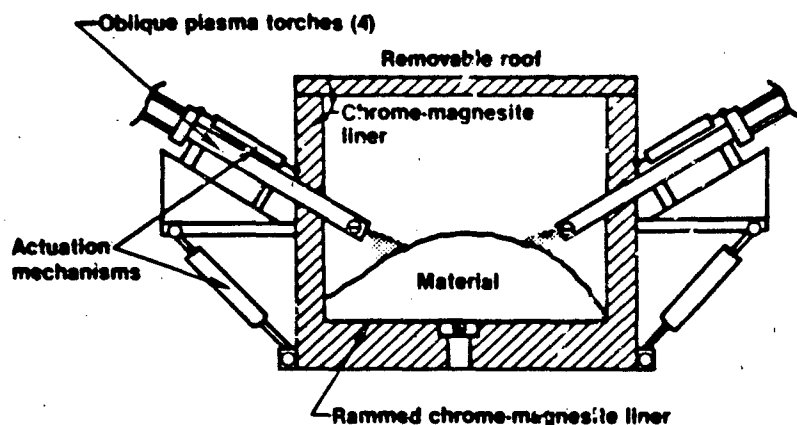
FIGURE 3-10 German Democratic Republic plasma furnace.

chrome-magnesite; the bottom section is lined with rammed chrome-magnesite refractory. Due to the high heat loads, several sections of the reactor incorporate water-cooled assemblies to provide long lifetime with minimum erosion. The number of high current (approximately 6,000 A) dc plasma sources used (nominally 3 to 6 independent units) depends on the reactor size and processing requirement. Depending on the number of sources used and the exact configuration, proper adjustment of the gas flow is required to counterbalance the electromagnetic forces between each plasma source positive column. The current level, column length, and separation distance are critical parameters that must be properly adjusted to obtain stable operation. Instabilities have been observed at low gas flows and relatively short positive columns. Resistance heating levels of the tungsten alloy cathode appear to be the dominant factor in influencing electrode lifetime. As in many other plasma cathode electrode configurations, the degree of cooling applied to the cathode is most critical in ensuring a long lifetime.

Additional details on the 10- and 30-ton plasma reactors are given in Table 3-7. It should be noted that the 30-ton unit's specific energy consumption is equivalent to updated electric arc furnaces. The efficiency increases with the size of the furnace and power input (e.g., 5-ton furnace 600 to 800 kWh/ton vs. 30-ton furnace, 500 to 550 kWh/ton). These large plasma reactors have additional advantages over high power electric arc furnaces. These include reduced melting times attributed to higher heat transfer rates; reduced melt contamination from carbon electrodes; very low residual oxygen and hydrogen levels; smoother power loading (no flicker or surges); high alloying species retention due to more controlled heat input and argon atmosphere; reduced total iron losses (less than 2 percent) due to inert atmospheric environment; reduced carburization from graphite electrodes as used in conventional arc furnaces; potential for insitu nitrogen gas phase alloying; and significantly reduced noise level.

TABLE 3-7 Comparison of Small-Scale and Large-Scale German Democratic
Republic Plasma Furnaces

Characteristic	Type P15	Type P35
Design capacity (tons)	15 (nominal 10 tons)	35 (nominal 30 tons)
Voltage (Volts)	700	700
Power (kW) (0.96 power factor)	10	20
Meltdown rate (tons per hour)	9	20
Specific energy consumption (kWh per ton)	600 nominal	500 nominal (equivalent to conventional arc melting process)
Argon gas flow (m^3 per hour)	18	45

Related activity with this type of refractory-lined plasma melting reactor
is also in progress in the Soviet Union [9]. In these units a typical
lifetime of the roof refractory lining is about 70 heats; approximately twice
this number of heats is achievable for the wall surface lining. The main
cause of the refractory degradation is attributed to thermal loading from the
radiation emitted from the plasma source.

Significant developments of large-scale thermal plasma reactors and
high-power (megawatts) plasma sources are also evident at Acurex,
Aerospatiale, ASEA, Hüls, MINTEK, Ontario-Hydro, SKF, and Westinghouse.
Details of some of these activities were reported at the 6th International
Symposium on Plasma Chemistry, Quebec, Canada, July 1983.

Different plasma melting reactor schemes have been devised to enhance the
residence times between the injected material and the plasma source. As an
example, Foster Wheeler/Tetronics uses a precessing plasma source technique
wherein the source is located vertically over a molten pool and the plasma
positive column is moved in the transferred mode via precession of the source
at about 30 rps [10]. An external motor drive attached to the source
connected to the roof of the chamber with a ball seal permits the prescribed
motion while providing a seal for inert gas operation.

Figure 3-11 is a sketch of the basic configuration. The anode attachment
can be either to a circular water-cooled electrode located at the periphery of
the chamber or directly to the surface of the molten material. This concept
is employed as a means of increasing the dwell time between the material being
introduced, via the feeding system and the plasma heat zone. This type of
furnace has been operated at power levels from 0.2 to 1.4 MW in various
extractive metallurgy applications. These include thermal treatment of sand
to facilitate direct leaching of silica from zirconia, reduction of magnetic
concentrates to iron using powdered coke as reductant, and concentration of
low-grade ilmenite ores. Additional applications include spheroidization of
nickel and iron powder (approximately 5 μm size) and removing copper from
copper-bearing minerals.
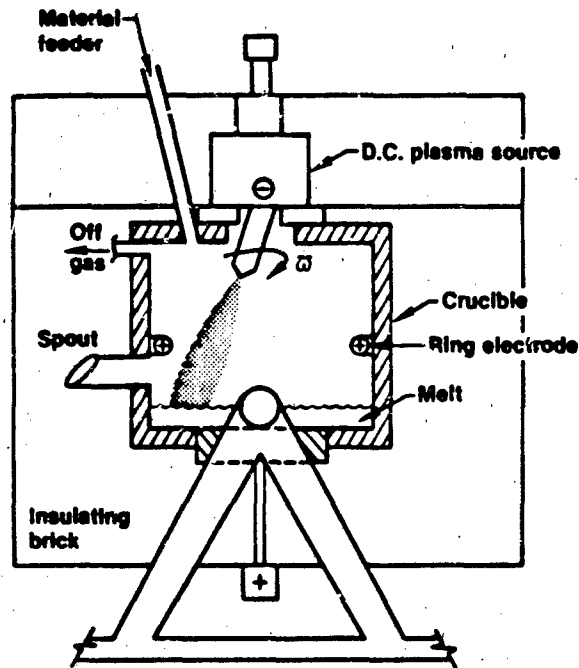
FIGURE 3-11 Foster-Wheeler/Tetronics plasma reactor.

The use of a closed-hearth-type extended carbon electrode plasma furnace
for the reduction of many types of oxide ore fines has been developed in
Canada [11]. Figure 3-12 illustrates the so-called extended arc flash
reactor. The hearth is formed within a magnesia refractory lining. Three
hollow graphite electrodes at 120 degree spacing supply the 3-phase power; gas
(argon, nitrogen, or hydrogen) injection is through the hollow electrode,
thereby achieving a relatively stable discharge. Pulverized oxide materials
are fed into the top of the flash column of the furnace by a rotary feeder.
As the fines drop through the rising hot gas stream into the zone of the
diffuse plasma, considerable preheating and prereduction occurs. Metals and
slag resulting from the reduction of the ores collect in the hearth and are
heated by radiation and convection from the plasma arcs. Batches of the metal
and slag can be periodically tapped from the hearth into molds. This type of
device could also be used for the reduction of various types of steel plant
waste oxides (e.g., those from basic oxygen furnaces, blast furnaces, arc
furnaces, and vacuum oxygen decarburization processes) to produce iron and
salable slags. Other potential particulate charges that could be treated
include steel mill dust, flue dust, mill scale, fly ash, and iron ore fines.
Reducing agents such as low-grade coal, anthracite, coke, or sawdust could be
mixed with the particulate charge. High-carbon ferrochromium has been
produced by reduction of low-grade chromite ores with a variety of reducing
agents in this type of furnace. The product was a high-carbon ferrochromium
($6.5 \leq C \leq 8.8$ percent) containing high levels of silicon and low sulfur and
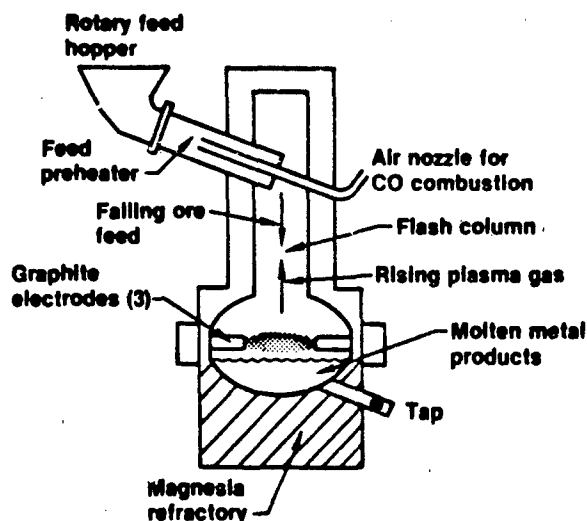
FIGURE 3-12 Extended plasma arc flash reactor.

phosphorous concentrations (1.8 $\leq$ Si $\leq$ 15.5 percent, 0.007 $\leq$ S $\leq$ 0.01 percent, 0.005 $\leq$ P $\leq$ 0.064 percent). Mixtures of argon, nitrogen, and hydrogen were used to stabilize the plasma; graphite or coke fines were the reducing agents. Metal recoveries between approximately 85 and 95 percent were achieved at energy requirements of about 13.2 kWh per kilogram.

Cold Crucible and Other Casting Systems

Different types of consumable and nonconsumable electrode designs are in use. The consumable-type systems are primarily employed in the melting and remelting of bulk-weldable electrodes and in the steel industry. The nonconsumable types are used primarily for scrap reclamation and consolidation. The most recent advances have been made with cold crucible nonconsumable electrodes coupled with continuous ingot withdrawal. Consumable-type systems are in commercial use in the Soviet Union for the production of nitrogen alloyed steels [9]. Figure 3-13 shows a design employing a hollow cathode [12]. The hollow cathode serves as a collimator and consumable nozzle to obtain a longer discharge with associated higher voltage levels. In contrast to typical VAR reactors with large shrinkage cavities, this design includes provision for an on-axis plasma source for hot topping.

Figure 3-14 shows another type of consumable electrode-plasma melting reactor that is in use in the Soviet Union [12]. In this system, a plurality of plasma sources are located in the sidewalls and are used to continuously melt a large consumable electrode that is rotationally indexed downward toward the mold assembly. Relatively short gaps are used in this geometry, with the plasma sources directed at the central region of the molten pool so that radiant energy from the superheated pool surface enhances electrode melting.
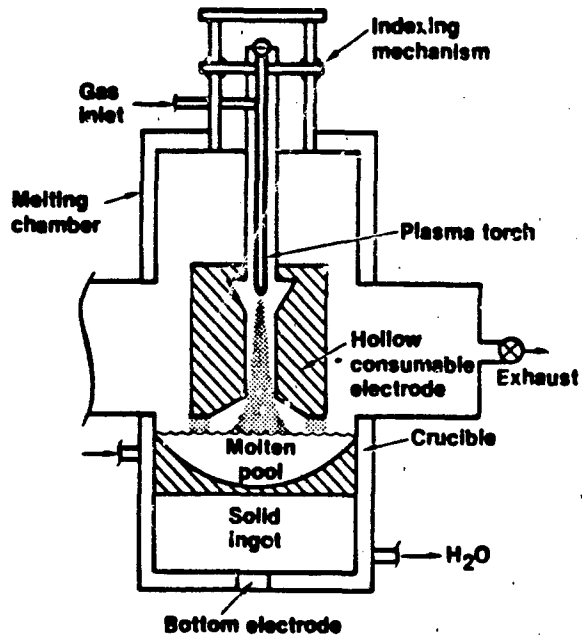
FIGURE 3-13   Soviet production scale plasma arc system for hollow electrode melting.
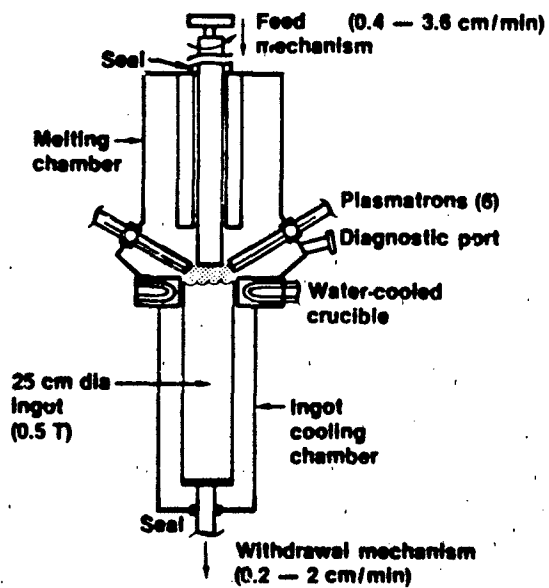
FIGURE 3-14   Soviet production scale plasma arc system employing multiple sources and continuous ingot withdrawal.

Use of a cold mold and controlled plasma heating assists in achieving the shallow melt profiles in this configuration that are conducive to good workability because of unidirectional grain solidification.

The nonconsumable plasma melting reactor with cold crucible and continuous ingot withdrawal has been developed primarily for scrap (solids, turnings, powder) consolidation into ingot material and subsequently into final working billet form via several VAR operations. Figure 3-15 shows the Daido plasma progressive casting (PPC) reactor with a single thermal plasma source [7]. In this single source configuration, the power level is about 0.1 MW and a 12-cm-diameter mold is used for continuous bottom withdrawal. Because of the strong affinity of titanium for oxygen and nitrogen, water-cooled copper molds with the plasm operating under approximately 1 atm of inert environment (argon) are employed. This system is used in the development of continuous ingot withdrawal technology using titanium sponge, scrap, commercially pure, and various alloy combinations thereof. The ingots produced are subsequently used as electrodes for follow-up VAR operations.
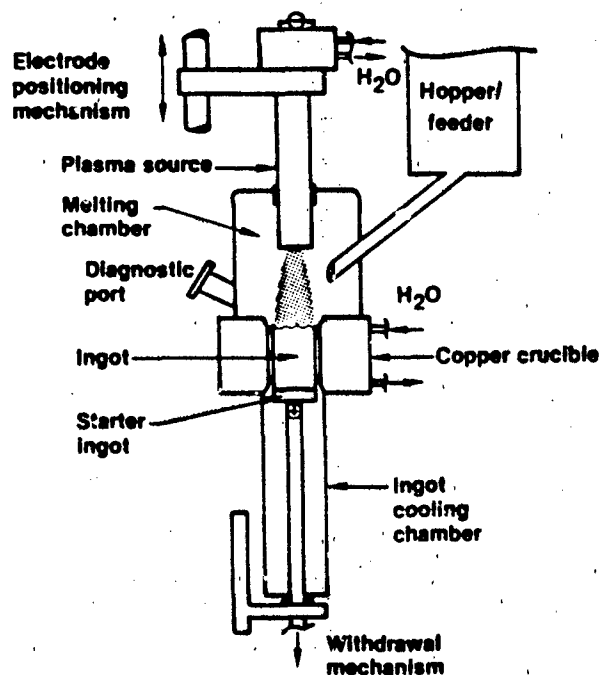
FIGURE 3-15 Daido plasma progressive casting furnance.

Figure 3-16 shows the basic plasma skull casting reactor (multiple plasma sources) that has been under development over the past 5 years [7]. This reactor is primarily used for producing castings of reactive metals and alloys. During the past year, Daido reconstructed the plasma skull casting reactor to be used also as a PPC reactor. Most recently, emphasis has been placed on trial production of various materials, including titanium alloys, with both processes. Several different multiple-plasma-source configurations are being investigated, but details are not available.
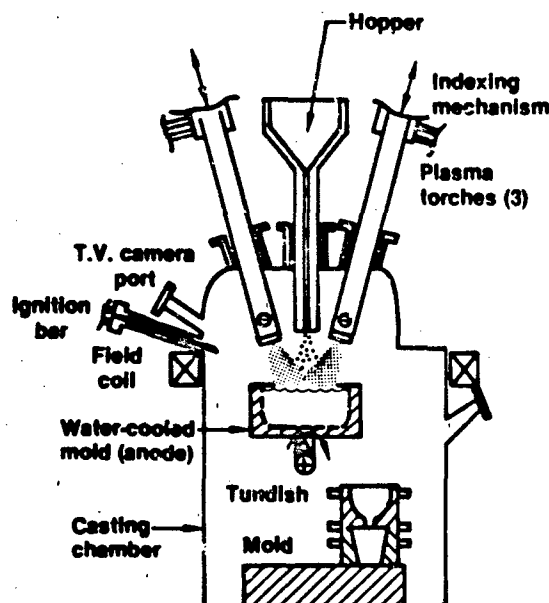
FIGURE 3-16 Daido multiple-plasma-source reactor for skull casting.

As an example of a state-of-the-art continuous casting system, some additional details on the basic operation are given here. The initial step consists of loading the material into the hopper. A combination rotary and mechanical booster pump evacuates the reactor to approximately 10^{-3} torr pressure. The reactor is then backfilled with argon to 1 atm pressure. A high-frequency starter in conjunction with an ignition starter bar system is used to initiate the plasma source. Removal of the starter bar while increasing the plasma current and argon gas flow rate transfers the positive column and anode attachment to the ingot. This part of the process is fully automated. The sources and ingot or crucible system remain stationary. A television camera system is used for continuous viewing of the molten pool and plasma column. Stirring, to induce homogeneity, occurs via use of a dc field coil integral with the mold assembly. Daido claims several unique characteristics of this type of reactor relative to vacuum arc or electron-beam systems, including operation in a 1-atm inert (argon) environment with negligible vaporization losses of the alloying elements, negligible loss due to molten pool splash by using a nonconsumable long-lifetime type of electrode system, use of a wide variety of scrap types and forms as the melting material, and achievement of a significant degree of superheat to the molten metal, thus leading to simplified production of thin-wall castings. Some recent testing is being directed to the production of reactive (and brittle) intermetallic compounds that have application for hydrogen storage. Normally the ingot serves as the anode (grounded side of power supply) when multiple plasma sources are used. The cathode is composed

of a conically-tipped thoriated tungsten (approximately 2 percent Th).
The exact geometry used, argon sheath injector design, cathode tip shape, and
degree of water cooling are important parameters in providing a stable,
uncontaminating, long-lifetime plasma source. Cathode tip lifetime is
reported to be 300 to 1,000 hours. Daido designs, manufactures, and markets a
wide variety of these plasma sources ranging in power leve from 30 kW to 1.2
MW. These units are designed for steady-state operation in a
transferred-type mode. Use of three plasma sources arranged radially
(120-degree spacing) provides a uniform melt zone. In addition to introducing
pool stirring, the application of external magnetic fields also serves to
deflect the positive columns to new locations on the pool surface and thus
aids in providing a uniform surface temperature at selected levels of
superheat.

Most of the products fabricated using the Daido plasma reactor are for
chemical, petrochemical, and nuclear applications. Fabrication of
nonaerospace ingot material has been demonstrated; qualification and
certification is pending.

To provide a comparison with Daido's PPC system, some details of a
competing plasma beam system operated by Nippon Stainless Steel, Ltd. for
melting titanium sponge and other alloys are provided here [13]. Nippon
produces stainless steel and titanium sheet, plates, strips, bars, wires, and
castings. Figure 3-17 shows the vacuum plasma beam furnace initially
installed 10 years ago in collaboration with Ulvac as a means of increasing
the smelting capacity of titanium and its alloys with the support of Sumitomo
Metal Industries Company Ltd. The titanium product size limitations are
nominally 1-m-diameter ingots. Five years ago Nippon received certification
of the material for pressure vessel applications. Most of the product is used
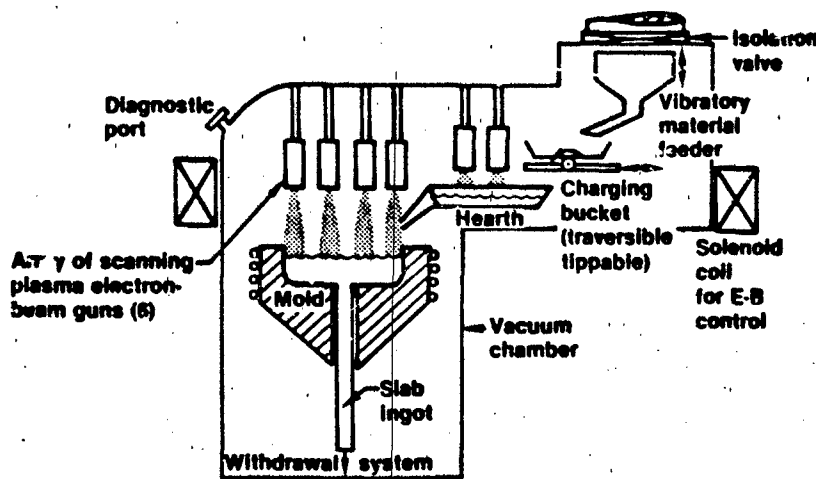
FIGURE 3-17   Nippon 2.4-MW plasma beam furnace for titanium slab ingot
               production.

in reactors, reformers, and heat exchangers. Nippon reports a production rate of approximately 10^3 tons per year as of 1982. To date, Nippon has produced over 5 x 10^3 tons of commercial slab ingots with the plasma beam system.

The 2.4-MW system shown by the sketch in Figure 3-17 has been developed to provide a direct conversion of titanium sponge into production-size slab ingots (0.75 to 3.5 tons), thus eliminating the preparation steps of primary and secondary electrodes and the secondary melting step as used in the standard vacuum arc melting process. The heart of the system is the six plasma guns (400 kW each); these are of the hot hollow cathode discharge type (as discussed earlier). The cathode material is tantalum. Nippon uses a rectangular water-cooled stationary mold and hearth. A vibration-type feed system is located within the large vacuum chamber (approximately 9-m high). A pivoting bucket system is used to intermittently charge the hearth and mold, in turn. The large plasma beam sources are scanned to eliminate localized superheat. An external magnetic field coil is used to focus the array of plasma beams; plasma beam distances are approximately 1 m. Typical operating conditions are 100 V and 3500 A; a relatively narrow stability corridor exists with this type of system. During actual melting, a large pumping system is required to maintain steady-state operating pressures of 10^{-3} to 10^{-1} torr. High-purity argon gas is required. The polarity selected is such that the slab is the anode. Typical slab withdrawal rate is about 0.6 cm per minute, translating to about 0.4 tons per hour for titanium slab ingots. Nippon indicates that close control of the plasma and melting parameters are critical to obtain dense, low-impurity slabs with good surface finish. It is during the completely molten phase of the melting operation at low pressures that element impurities such as magnesium, chlorine and hydrogen are reduced. Overall results indicate that the one-step conversion of titanium sponge to slab is comparable to vacuum arc double melting. In general, the "as cast" ingot consists of large columnar crystals at the extreme top portion (a shrinkage cavity is present if a hot-topping procedure is eliminated). Up to 100 percent scrap dosages have been processed, but a 40 percent dosage of scrap is nominal. No results have been reported regarding titanium alloy melting and processing conditions, but future plans include alloy processing.

Nuclear Waste Processing

The Daido Takakura works uses a modified thermal plasma system for reprocessing nuclear wastes. Six large power companies have been involved for several years in cosponsorship of this development program. The main objective is the volume reduction (approximately an order of magnitude) and stabilization of the noncombustible solid wastes generated at the various nuclear power plants. Figure 3-18 shows the basic thermal plasma melting furnace and solidification chambers [7]. The processing capacity of the developmental reactor is about 200 tons per year using a total plasma power of 310 kW. The entire system is located within a 10-m x 15-m x 15-m-tall building. In the solidification chamber three types of forms are being generated: 0.3-m cubic blocks, shot (0.1-cm to 0.7-cm-diameter), and direct solidification into a storage can. The thermal plasma characteristics of high-temperature, long-run-time stable operation at atmospheric pressure and nonconsumability of the tungsten electrode have provided relatively easy and complete melting of all metals (including those with high melting points),
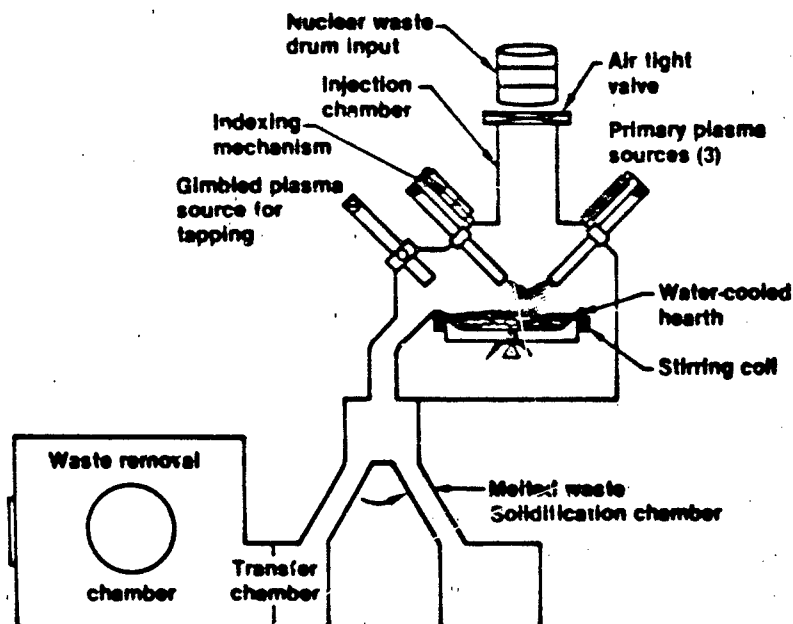
FIGURE 3-18   Daido Steel Company plasma reactor for nuclear waste
consolidation.

inorganic materials (glass, asbestos, concrete, etc.), and organic materials
(rubber, vinyl, etc.). The overlying advantage of using the thermal plasma
for this type of melting and consolidation process is the independent control
of the primary heat source relative to other systems. A separate 80-kW plasma
source is used in conjunction with a water-cooled hearth system to allow
continuous pouring of the molten waste. The input nuclear waste material is
contained within sealed 50 liter drums that enter a vertical feed chute
through an airtight valve system. During steady-state operation, the waste
gas generating rate is comparable to that from the array of plasma sources and
within the limits where standard off-gas exhaust treatment can be employed.
"Fines" generation is typically less than 1 percent of the total waste. The
maximum melting capacity is 4 tons per day.

Monocrystal Growing Systems

The Soviet Union has had a continuous and intensive developmental effort
in the area of thermal plasma reactors for melting and other special
applications. Included is the production of large monocrystals of refractory
metals, directionally solidified eutectic alloys, and high-melting-point
carbides. The primary effort in this area, in progress throughout the past 7
years, is being conducted at the Baikov Institute [14]. A sketch of the basic
apparatus is shown in Figure 3-19. Commercial applications of this type of
system have been activated throughout the Soviet Union.

The basic operation of the system shown in Figure 3-19 begins with fusing the end of a seed crystal using the plasma source itself. The molten materials are supplied by plasma melting of corresponding alloy metal (compacted or hot isostatically pressed) from small-diameter (typically less than 1 cm) feedstock. Continuous withdrawal of the ingot is conducted simultaneously with the solidification of the melted material on the top of the crystal. The gas composition consists of argon-helium and argon-hydrogen mixtures; the hydrogen constituent is used in the refining step. In lieu of feeding a consumable electrode in this process, pulverized chips or powder can also be used as the metallic charge in this monocrystal growing of refractory metals. Reported results reveal that relatively large-diameter circular and rectangular monocrystal ingots of tungsten have been produced possessing excellent physical properties, especially the property of ductility at normal temperatures. As an example, tungsten monocrystal slabs were rolled into plates at temperatures 1000 K lower than those required for powder-metallurgy-type hot-worked and rolled ingots. Monocrystal ingots of TiC, HfC, and NbC have been produced via the thermal plasma systems when gases such as CH_4 and CO_2, to react insitu with the melt, are employed as the source of the carbon for these high-melting-point carbides. The distinct advantages of this thermal plasma approach over other competing systems such as electron beam and vacuum arc reside in its compact simple design coupled with its energy-efficient, simplified mode of control and operation with a wide variety of gases.
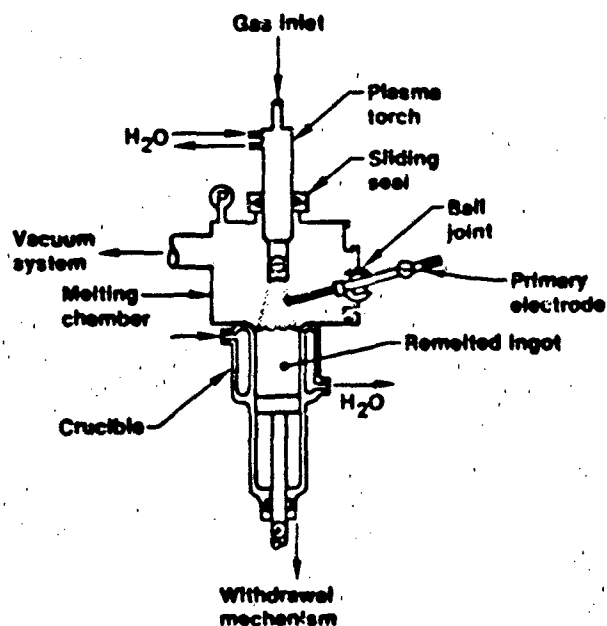
FIGURE 3-19 Soviet plasma reactor used in monocrystal growing.

Plasma Surface Treatment Systems

Before the hot and cold working and machining steps to billets and ingots as prepared by different primary and secondary operations, surface preparation and treatment are required. This operation is needed to repair surface cracks, protuberances, and other blemishes (e.g., arc material splatter from VAR processing of bulk weldable electrodes) that have occurred in the prior processing steps. The ability to smooth the outer diameter surface and improve the surface condition and concentricity to within designated specifications alleviates the need for the use of expensive centerless grinding equipment and other types of surface-treatment equipment (e.g., electric discharge machining, pickling, alkaline bath, chemical etching). The amount of material that can be saved from being converted to waste metal scrap, chips, or grinding sludge and/or subsequently downgraded is significant compared to the cost of a plasma surface treatment system.

The environmental pollution regulations in the United States are rigid with respect to the handling and final disposition of grinding swarf and chemical treatment waste, and therefore application of plasma melting technology for surface treatment would be beneficial in this area.

The basic operation of plasma surface treatment, similar to a laser glazing operation, consists of locally melting a relatively thin layer of material in a continuous operation. A controlled localized heating operation can also be incorporated with a cutting machine operation or an auxiliary gas jet can be directed on the locally melted layer to effect direct material removal (as in oxy-acetylene cutting operations).

Development of plasma surface treatment equipment is currently being conducted in the Soviet Union [12]. Figure 3-20 shows the type of equipment presently being used for surface treatment of steels, specialty steels, and titanium. A chamber large enough to contain the entire billet form is normally operated under an inert atmosphere environment. The billet is supported on a series of mechanically actuated rollers that allow controlled rotation of the billet while being exposed to a series of plasma sources that are axially scanned over the periphery of the rotating billet. The horizontal orientation is used to facilitate the ease of loading and unloading the large billets.

STATUS OF SCIENCE BASE

Based on the information presented in this report and on personal communications with researchers in the field and with operators of laboratory-scale, pilot-scale, and production-scale plasma reactor hardware used for melting applications, thermal plasma arc technology for melting and remelting operations has indeed become established in several fields of commercial application.

Examination of the accumulated data base shows that Japan, the Soviet Union and the German Democratic Republic are taking a leadership role in pioneering the operation of large-scale plasma reactor systems for melting applications. The reestablishment of the United States in a leadership position in this high-technology area is important both for our economic
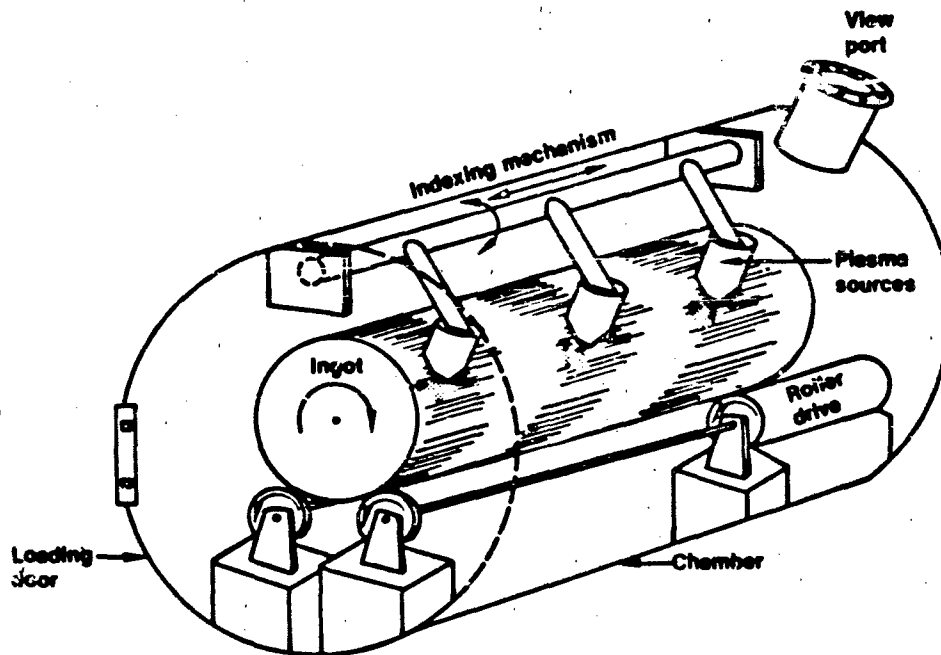
FIGURE 3-20 Soviet plasma system for surface treatment.

health and for our security in strategic materials. Throughout the world, industrial furnaces of all types consume about 50 percent of the energy resources produced in the world, and thus the impact of converting even a small percentage of these furnaces to efficient thermal plasma reactor types is very significant.

With only a few exceptions (as noted in this report), thermal plasma melting technology in the United States is still in the laboratory or pilot-plant stage, whereas in foreign countries a variety of full-scale production systems, operating at steady-state process power levels up to about 20 MW, are in continuous operation. The importance of thermal plasma technology for melting applications is apparent from the foregoing overview and discussion of representative applications. Thermal plasma melting and materials processing is an interdisciplinary technology in transition. New prospects for large-scale implementation of plasma melting technology by the domestic mining, metallurgical, iron and steel, speciality metals, and chemical industries appear most promising, based on some of the recent state-of-the-art advances described.

Much of the science base that is available in the literature deals with plasma welding, cutting, and to a lesser extent plasma spray torches. Unfortunately, many of the large-scale reactors that have achieved commercialization are operated in a proprietary manner. From the examples described in this report, it can be assumed that a reasonable level of technical understanding is available for several of the important thermal plasma melting reactor systems.

The majority of the basic research and development studies appearing in the literature are of plasma cutting and welding technology. The successful design of future production-scale thermal plasma reactors for melting/materials processing applications will require a broad understanding of the heat transfer aspects, transport properties, and reaction kinetics of very high temperature multiparticle systems. Research in thermal plasma melting technology to date has been strongly oriented toward technical feasibility studies for the development of a specific process (in many cases proprietary, unpublished information). There is a definite need for research to close the existing gap between the fundamentals of thermal plasma technology and the physics and chemistry of process metallurgy. The overlap of several disciplines suggests that an interdisciplinary approach will be required to further the understanding of this complex but important technology. With this type of approach, it may be possible to see before the end of this century the manufacture of basic products such as steel, fertilizer, silicon, acetylene, cement, and new superalloys benefiting from large-scale developments in plasma technology.

The following examples illustrate the fundamental long-range research required to progress technically in thermal plasma melting technology.

- Investigation of nondeteriorating (nonconsumable) electrodes capable of steady-state long-lifetime operation at high current levels. Included should be determination of critical failure mode, the effects of electrode design, composition, and cooling on electrode performance and lifetime, and the effects of key operating parameters on electrode erosion. This information will eliminate cross-contamination and process downtime.

- Improved systems for introducing, in a continuous and reproducible manner, controlled amounts of feedstock to be melted or processed. This includes studies of the physical interaction of materials (solids, chips, powders) injected into and entrained in the plasma discharge-molten pool interface region and potential advantages of pretreatment or preheating of feedstock, as well as improved quench techniques to permit efficient product separation.

- Fluid dynamics and thermal modeling of the plasma system. Emphasis here should be on mathematical models for gas flow field, electromagnetic force field, and temperature field in dc transferred arc mode plasma systems, and on modeling of the molten pool-ingot-crucible interface heat transfer and macroflows within the molten pool.

- Determination of the physical limitations to high throughput of material. This includes the feeder system, plasma heat source, hearth or crucible, and ingot withdrawal system. Optimization of the system should be sought for maximum ingot withdrawal rate combined with improved techniques for achieving completely dense, homogeneous final ingots with minimum erosion and contamination and with good surface finish.

- Investigation of new techniques for complete removal of inclusions (low-and high-density) from processed material. This should include the use of material pretreatment, cleaning, segregation schemes, and hearths for settling or floating out deleterious material, as well as determination of trace element buildup resulting from increased utilization of recycled materials.

- Investigation of absorption and desorption of plasma species by metal melts, including determination of reaction mechanisms and rate coefficients. Also included should be secondary refining processes for decarburization, deoxidation, and alloy additions involving combination of injection metallurgy techniques with a thermal plasma-heated carrier gas.

- Identification of key parameters for achieving clean melts, fine grain size, and improved microstructure of dense ingots. This includes investigation of effects of plasma discharge heat flux distribution, prescribed discharge motion on molten pool, influence of external magnetic fields on mixing, and heat transfer losses to mold and crucible systems.

- Establishment of new techniques for material pretreatment and contamination identification and removal. Included here are both passive and active diagnostic systems for on-line identification of elemental constituents, contamination, and distribution of contamination (surface or bulk) in input feedstock. Novel combined chemical-plasma techniques for contamination removal from strategic materials should also be investigated.

- Investigation of physical metallurgy of thermal plasma surface treatment and glazing. This includes characterization of different plasma modes (i.e., transferred, nontransferred) relative to local surface melt efficiency and heat transfer losses as well as determination of operating parameters for optimized workpiece surface treatment and maximum processing rate.

- Modeling development to predict scaling from laboratory-size thermal plasma melting reactors (typical 5-cm-diameter ingots) to production-size plasma reactors (typically 45-cm-diameter ingots or slabs). This should include detailed heat transfer analysis and sensitivity analysis to variations in operating conditions.

The following are examples of critical developmental needs and engineering studies required for rapid technical progress in thermal plasma melting technology.

- Establishment of pilot-plant-scale demonstration equipment and full-scale production hardware optimized for a specific application so as to provide highest product yield at minimum cost. This includes optimization of feedstock form and throughput, plasma source configuration and operating mode, on-line diagnostics for monitoring input material, contamination limits, and quality of the final

product relative to specification, as well as possible interface with current automated computer-controlled feedback and control systems and robotics.

- Detailed economic analysis of several selected technically feasible thermal plasma processing systems. This should include sensitivity analysis of raw material costs, electrical costs, equipment utilization, overall efficiency, and related considerations.

- Detailed engineering evaluation of thermal plasma melting systems relative to alternative competing technologies (e.g., vacuum arc remelt, electron-beam, plasma beam, electroslag remelt).

TECHNOLOGICAL OPPORTUNITIES

A challenge exists for improving the efficiency of energy utilization and conversion and providing new innovative plasma technology methods for metals extraction, melting, remelting, refining, and recycling of materials.

Thermal plasma reactors are compact systems that can process material in a variety of forms (e.g., solids, chips, powder) at high throughput rates and with relatively high electrical and thermal efficiency. In an era of growing awareness that conservation of materials must be pursued in an efficient and cost-effective manner, new thermal plasma processing techniques are being considered throughout the metals processing industry in converting the raw material into ingot-type products.

Incorporating many of the advantages mentioned, the following is a list of key technological opportunities for thermal plasma melting technology.

- Cold crucible melting and recycling of strategic scrap material using continuous ingot withdrawal techniques. This includes melting metals and alloy scrap in the form of solids, turnings, and powders into a dense, reusable ingot that is within physical and chemical specifications.

- Consolidation, alloying, and blending of nonstrategic scrap into bulk weldable electrodes as used in secondary vacuum arc remelting.

- Casting production of reactive and volatile metals and alloys and preparation of alloy master melts.

- Production of large monocrystals of refractory metals, directionally solidified eutectic alloys, and high-melting-point carbides.

- Production of ultraclean superalloy powders as used in aerospace applications; production of new refractory powders for high temperature ceramic applications.

- Reprocessing of nuclear wastes for volume reduction and stabilization of the noncombustible solid waste.

- Toxic chemical waste treatment and decomposition of hazardous wastes into simple compounds for subsequent scrubber and flare treatment.

- Production of nitrogen-alloyed steels via plasma injection technique as a substitute for chrome steels.

- Ingot, casting, and slab surface preparation and treatment prior to secondary grinding processing.

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Chapter 4

PLASMA EXTRACTIVE METALLURGY

The extraction and refining of most metals takes place at temperatures ranging from 1273 to 1773 K because of their elevated melting points and the thermodynamic criteria for the decomposition of ores. When these temperatures are in excess of 1673 to 1873 K, the use of electrical energy in the form of arcs, submerged arcs, or submerged resistance heating, rather than the direct employment of fossil fuel, is generally the most efficient way to carry out the extraction process.

Reactors using thermal plasmas as the energy source, however, may be logical candidates for replacing some of these technologies. The main attraction of plasma reactors in smelting, melting, or refining operations is their ability to supply a concentrated high-temperature heat source, which allows for a high processing rate per unit reactor volume.

In spite of this there have been very few industrial-scale applications of plasma systems in extractive metallurgy, although many possible applications have been suggested. These include the smelting of virgin ores, calcination, preheating of gases and feed materials to augment existing processes, and specialized melting systems for the recovery of fine materials combined with ore reduction.

A detailed description of plasma reactors and of the plasma characteristics relevant to extractive metallurgy processes was given previously in this report [1]. Hence, this chapter will focus on the potential role of plasma technology in light of the needs of the extractive metallurgy industry and show that in many instances there are important opportunities.

FUTURE NEEDS IN EXTRACTIVE METALLURGY

Extractive metallurgy is defined as the winning of metals in their pure or usable alloy form from ores. In exploring the impact of plasma processing on the extractive metallurgical industry, we should note that the production of iron and steel has increased threefold [2], aluminum increased elevenfold, copper and zinc have nearly tripled, and lead has doubled in the last 30 years [3]. Since 1946, 17 times as much aluminum and twice as much copper and zinc

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have been produced than in all prior recorded history. The U.S. Bureau of Mines predicts annual metal production growth rates ranging from 5.5 percent (aluminum) to 2 percent (zinc) to the year 2000. This continued growth confronts the industry with broad social issues. In the past, abundant low-cost energy, relatively small quantities of waste material, and the abundance of relatively rich ores resulted in few problems for the metals industry; it simply expanded to meet the needs. But today the high cost of energy, the greater awareness of waste being generated, and the depletion of rich mineral resources have led to four major problem areas facing the extractive metallurgical industry:

1. Energy conservation—resulting from the high cost of clean energy sources since the oil embargo of 1973.
2. Capital intensity—resulting from the very large scale operations necessary for good return on investment coupled with high risk, high capital requirements, and high interest charges.
3. Environment and worker health—resulting from larger quantities of waste—both solid and gas—generated by the expanded conventional processes as well as the recently discovered hazards to health that must be addressed.
4. The need to process low-grade complex minerals and to process domestic ores of strategic metals—resulting from the depletion of the richer naturally concentrated ores [3].

Increased scrap recycling addresses all four of these problems since it requires much less energy and capital investment to recover material already in the metallic form. Environmental problems, worker health, and processing of low-grade complex minerals are alleviated to the extent that the extraction of metals from these minerals is avoided. This may be the first effective area for plasma processing to enter the extractive metallurgical industry. It could be applied to the recovery of high-value metal from waste dusts, through the melting of lower valued metals for recovery, and progressing to new processes resulting in the separation of the metals.

Energy Conservation and Capital Intensity

Energy and capital costs cannot be easily separated in the extractive metallurgical industry because one is frequently traded for the other, particularly where the use of lower cost energy requires expensive environmental controls. At the International Centennial Symposium of the U.S. Geological Survey [4] it was predicted that the supply, demand, and cost of energy will be the overriding resource problems of the 21st century. The production of oil and natural gas may well pass its peak by the year 2000, and the time to develop advanced nuclear technology and discover further supplies of nuclear fuel must be bought by the ample coal supply. Ultimately, available energy will be primarily electric, which may well be the abundant and cheap fuel by the standards of the future economy. World deficits by the year 2000 of such metals as germanium, indium, mercury, silver, and zinc —predicted by the U.S. Bureau of Mines—will require more energy to process the remaining small mineral deposits and low grade ores to produce these as well as many of the other metals. This in turn will mandate the development of less energy- and capital-intensive processes for metals production.

Due to the inherent inefficiency of generating electricity in a fossil fuel plant, the overall fuel-to-electricity-to-final-use efficiency can seldom exceed 30 percent. Although present fuel-burning extractive metallurgical processes frequently operate at lower efficiencies than 30 percent, it is possible to bring them to the 40 to 80 percent efficiency range with careful design and additional capital investment. Therefore, electricity should be selected for basic processing only when there are certain specific requirements:

1. Temperatures exceeding those possible with fossil fuels (greater than 1873 K, where with fossil fuels less than 30 percent of the energy is available for processing) are necessary for the reaction.
2. No process other than one requiring electrical energy is known; or
3. Electrical energy permits the use of an integrated process that yields a variety of products and shows total energy conservation and capital reduction offsetting increased energy cost.

There are many opportunities for plasma processing that meet these criteria. However, economics mandate the use of as much fossil energy as possible, either to reduce electrical input or to produce such useful gaseous by-products as the carbon oxides and hydrogen. For instance, in the electrolytic production of zinc from aqueous zinc sulfate, methanol additions to the electrolyte result in carbon dioxide evolution rather than oxygen, and in the Hall process for aluminum production, consumption of carbon at the anode reduces the electrical energy input by approximately 10 percent through production of carbon dioxide instead of oxygen. Introducing carbon as a reductant in high-temperature plasma processing permits the sale of carbon monoxide as a by-product, increasing energy efficiency and decreasing cost.

Environmental Control and Processing of Low-Grade Ore

The rapid increase of waste products that must be treated for safe disposal for the protection of the environment and worker health will be aggravated in the future by the need to process leaner ores that yield greater quantities of waste materials per pound of metal produced. The most cost- and energy-efficient way to solve these problems would be to totally enclose the system and use the gaseous and solid wastes as feed for other processing systems that produce valuable products.

Such integrated industrial complexes would also result in energy conservation and reduce capital requirements per annual ton for each commodity produced. Plasma processing techniques lend themselves most readily to the development of metal-separating processes as well as to a system where, through a series of high-temperature treatments under properly controlled atmospheres, first the volatile oxides would be removed, followed by carbon reduction of the remaining material into two separate phases, one metallic and the other an oxide mixture that would subsequently be processed to produce the remaining metals. If the ore selected is also a waste product that is already an environmental problem, such as fly ash, the economics could become particularly attractive.

An example of such a system would be an integrated process to produce a variety of products, including electrical energy, aluminum, ferrosilicon,

magnesium, sulfur or synthetic gypsum, cement and carbon monoxide for organic synthesis. Raw materials would include coal, limestone, dolomite, and some makeup salts for electrolysis. Although clay, anorthosite, or shale residue could also be used for this process, the elimination of waste material by converting it to useful products becomes more attractive, particularly if it replaces imported materials [5-11].

More than 700 million tons of coal are used in the United States each year, primarily for electric power production. By 1990 consumption may be as high as a billion tons per year. Some 10 to 15 percent of the bituminous coal is ash, 15 percent of which leaves the bottom of the grate as boiler slag and 85 percent of which is blown out of the stack as fly ash (spherical particles ranging from 0.5 to 100 microns in diameter). One hundred million tons per year are available for processing and would yield, if a 100 percent conversion were possible, 9 percent of the U.S. needs of iron, 221 percent of aluminum, 400 percent of magnesium, and 2000 percent of titanium [12]. One large generating station is in operation that could produce 350,000 tons per year of aluminum oxide from 1.2 million tons of ash per year [13]. If only 70 percent were recovered, 125,000 tons per year of aluminum could be made. A modern plasma processing system using fly ash could be energy efficient, might be modified to effect better separation of constituents, and would produce by-product carbon monoxide for organic synthesis. One hundred million tons of fly ash per year could, in principle, provide a substitute source for all of the aluminum consumed in the United States, 40 percent of the iron ore imported, and all imported ferrosilicon.

An integrated system using plasma processing for the more difficult separations, where all process wastes are used as raw materials for other processes, would solve most of the problems besetting the extractive metallurgy industry today.

Advantages, Problems, and Applications of Plasma Processing [14-17]

As applied to extractive metallurgy, the plasma furnace is a totally enclosed, high-temperature-chemical reactor involving thermodynamic equilibria, reaction kinetics, and heat transfer as contrasted with a melting furnace where the primary consideration is heat transfer.

ADVANTAGES OF PLASMA PROCESSING

There are numerous advantages of plasma processing applied to extractive metallurgy.

1. Controlled furnace atmosphere: In a plasma reactor the atmosphere can be controlled to meet nearly any process requirement because its design and materials of construction make it compatible with almost any gas--reducing, oxidizing, or inert.

2. Reduced capital intensity: High reaction rates and heat transfer at plasma temperatures, coupled with high massless energy release, permit high feed rates of reactants and short residence times and allow reduced complexity, improved energy efficiency, and reduced capital cost.

3. High temperatures possible: Plasma reactors can operate at high temperature with more available energy than reactors fired with fossil fuels. Using arc heated air at 4000 Btu/lb, 40 percent of the energy is available for processing at 2480 K as compared with only 1530 K for a natural-gas flame at the same available energy efficiency. Direct arc temperatures are availabl. from 6000 to 20,000 K as compared to a maximum natural-gas flame temperature of about 2280 K with no energy remaining for processing [17].

4. Versatility: All forms of matter can be processed in a plasma reactor. Bench-scale and pilot processes involving the reaction of solids, liquids, and gases in any combination have been demonstrated successfully in plasma reactors.

5. Total enclosure: Plasma reactors may be operated as totally closed systems, thus avoiding contamination of the products and the capture of all volatiles. This is particularly advantageous if by-product carbon monoxide and/or condensed oxides or metals are to be filtered as a product from the effluent.

6. Controlled operation: Steady-state flow of high-temperature gases permits reaction control in a narrow range of temperature and residence time.

7. High electrical efficiency: The compact nature and high heat release and transfer permit high conversion of electrical energy to heat energy and result in good overall efficiency if the heat energy in the products is recovered in some manner.

8. Ability to process finely divided material: Lower grade, finely divided powders may be reacted in plasma systems without sintering or agglomeration and with no loss due to oxidation or other reactions.

9. Electrical energy intensiveness: At sites where hydroelectric or nuclear power is available (France, Brazil, etc.), dependence on fossil fuels may be decreased.

10. Rapid quenching: The production of meta-stable states in new products may be achieved through ultra-rapid quenching made possible by high thermal gradients between the plasma arc and the surrounding gas.

Heat fluxes as high as 16 kW/cm^2 are possible in a transferred dc arc as compared to 4.5 kW/cm^2 in an argon jet and only 0.3 kW/cm^2 in an oxygen fossil fuel flame. Heat transfer is enhanced by high velocities, high plasma gas thermal conductivities, and high temperatures [16-18].

DISADVANTAGES OR PROBLEMS TO BE SOLVED

Although high temperatures result in high reaction rates in plasma reactors, a number of inherent problems must be resolved to make plasma processing economically attractive.

1. Heat recovery: The reactants are easily and efficiently heated to reaction temperature, either by preheating with a cheaper energy form or by carrying them from room temperature to reacting temperature in the reactor itself. After the reaction is complete, however, the products contain a high potential energy level in the form of latent heat. If a large fraction of this heat is not recovered as electrical energy or preheat for future reactants, the resultant thermal inefficiency makes the process economically unattractive. Means must be developed to recover this energy, perhaps as high pressure steam or in gas turbines, in a similar manner to the recovery of blast furnace heat to meet on-site electricity requirements.

2. Electrode life: Reacting systems that have a high percentage of on-stream time with minimum maintenance costs during down times have significant advantages over competing processes. Although electrode costs and labor costs for changing them are important, the paramount reason for longer electrode life is continuous operation, which yields high productivity and low labor, maintenance, and capital costs. Electrode life in some plasma heaters is purported to be as high as 300 to 400 days under ideal conditions, but this life probably cannot be maintained at the high temperatures and more severe conditions required for plasma reactors. Since some electrode melting and vaporization are inevitable, particularly at the high temperature conditions necessary for some of the more desirable plasma applications, development of lower cost, longer life materials will be essential to the development of economically viable processes.

3. Residence time: Despite the high reaction rates at the temperatures envisioned, it is unlikely that high yields can be obtained in in-flight reactions. Some means of swirling, baffling, or extended reaction chambers are necessary to give the reacting solids sufficient time at appropriate temperatures and pressures to result in high yields. These problems should be much less acute with gaseous or liquid reactants. Much work has been done in this area, but plasma reactors are process-sensitive, requiring specific reaction chamber designs for each use.

4. Rapid product quench: Many dissociation reactions envisioned as possible applications for plasma reactors require rapid cooling below some critical temperature to obtain high yields and avoid back-reaction to the original reactants. An example of this problem is the reduction with carbon of aluminum oxide or magnesium oxide to metal vapor and carbon monoxide. In the case of aluminum, if products of the reaction are not quickly lowered from 2570 K (required for reaction) to 2075 K, where aluminum condenses at 1 atm, the aluminum vapor will back-react with the carbon monoxide to produce the original reactants-alumina and carbon. In magnesium production this problem was solved in the Hanskerg process by rapidly cooling the magnesium vapor and carbon monoxide with a cold jet of hydrogen [19]. This method did not result, however, in recovery of the thermal energy in products, and the process lost out to electrolysis.

POSSIBLE APPLICATIONS

In examining possibilities for applying plasma processing to extractive
metallurgy, the information in Table 4-1 and Table 4-2 provides useful
perspectives. The 3-year spread for production and pricing given in Table 4-1
is necessary to avoid the distortion that took place in the recession year of
1982 [20-22].

It is known that iron and steel are the most used and needed metals in
society, since their world production is 20 times that of the next most needed
and used metal, manganese (over 50 percent of which is closely tied to the
iron and steel industry as an alloying agent). The production of aluminum,
the second most important structural metal, is only 1/30 that of iron and
steel, although in the United States it is about 1/15. If need, as measured
by consumption, were the only criterion for the selection of possible
profitable applications of plasma technology, first consideration should be
given to iron and steel followed by manganese, aluminum, chromium, copper,
zinc, lead, nickel, magnesium, tin, and titanium in that order. Another
important criterion would be the net import reliance of the United States for
the metal in question. Table 4-3 is a prioritized list of strategic metals
[23].

Iron oxide reduction in a single step using hydrogen or methane as the
reductant has many advantages. In such a process electricity would be used
for heat, process energy, and the production of the hydrogen reductant from
natural gas or coal. Production of costly metallurgical coke would be
avoided, and carbon- and oxygen-free iron would be produced in a totally
enclosed system, reducing pollution control measures and yielding a product
from which steel could be made in simplified processing steps. Such a process
has been demonstrated technically at a 1 MW-pilot scale [14,17]. It is rather
unlikely, however, that plasma technology will be used for the smelting of
iron ores on a tonnage scale, except for special applications. The reasons
for this are as follows:

- The overall energy requirements of producing steel in plasma reactors
  are estimated to be 2000-3000 kWh/ton considerably more than
  conventional technology.

- Additional problems are posed by the unavailability of the plasma
  torches needed for such an application (in the 40 to 100-MW range).

- Finally plasma smelting of ferrous ores should not be compared with
  the existing steelmaking technologies but with the new ideas for
  fossil fuel-based direct smelting systems, which could offer
  comparable advantages to plasma smelting without the drawbacks
  mentioned here.

These considerations will not apply to scrap melting with plasma guns, a
technology practiced by Voest Alpine in Austria, or for some special
situations, such as in Sweden, where local circumstances encourage the
development of such operations.

TABLE 4-1 Production of Metals

Metal	Present Process	U.S. Production (millions of short tonnes)			World Production (millions of short tonnes)			Average Price Range ($/lb)		
		1980	1981	1982	1980	1981	1982	1980	1981	1982
Iron & Steel	Blast furnace charged with iron ore, coke, limestone	69.4	74.2	44.0	559.7	552	506	0.101	0.102	0.106
Manganese	Blast fce; aqueous electrolysis	0	0	0	29	26	23	1.60	1.70	1.60
Aluminum	Fluoride electrolysis of alumina	5.1	4.9	3.6	16.9	16.6	14.6	0.72	0.76	0.76**
Chromium	Reduction of chromic oxide; electrowinning	0	0	0	10.7	10.2	9.7	4.00	4.10	4.10
Copper	Electrolytic deposition; pyrometallurgy; electrowinning	1.3	1.7	1.2	8.4	9.0	8.6	1.02	0.85	0.74
Zinc	Retort; electrothermic; blast furnace; electrowinning	0.35	0.34	0.33	6.3	6.4	6.8	0.37	0.45	0.38
Lead	Sintering; blast furnace smelting; refining	0.6	0.55	0.56	3.9	3.7	3.8	0.43	?.37	0.26
Nickel	Concentration; roasting; converter; electrolysis	0.015	0.012	0.0032	0.85	0.77	0.58	6.70	3.30	3.20
Magnesium	Chloride electrolysis; silicothermic reduction	0.17	0.14	0.13	0.35	0.33	0.30	1.20	1.30	1.30
Tin	Reverberatory furnace smelting; blast furnace smelting	0	0	0	0.27	0.28	0.26	8.10	6.90	6.30
Titanium	Kroll Process; reduction of titanium chloride with Mg	0.023	0.026	0.018	0.069	0.10	0.083	7.02	7.70	5.60
Cobalt	Concentrating processes from metal extraction	0	0	0	0.033	0.034	0.033	25.00	21.10	14.90
Cadmium	Zinc retort; copper, lead smelting plants; electrolytic plants	0.0017	0.0018	0.0013	0.02	0.020	0.019	2.80	1.90	1.10
Lithium	Chemical extraction from spodumene	-- Proprietary --			0.0022*	0.002*	0.0017*	20.70	23.40	21.70
Gallium	Sodium alumina extraction; electrodeposition	-- Proprietary --			0.000013 / 0.000022	0.000013 / 0.000022	0.000022	231.00	272.00	286.00

* Excludes U.S. production
** Quoted price; spot price as low as $0.46/lb

TABLE 4-2 Ferroalloy Production (millions of tons)

Metal	U.S. Production		World Production	
	1980	1981	1980	1981
Ferromanganese	1.9×10^{-1}	1.9×10^{-1}	5.2	5.3
Ferrosilicon	6.8×10^{-1}	6.9×10^{-1}	3.4	3.6
Ferrochromium	2.2×10^{-1}	2.4×10^{-1}	3.4	3.5
Ferrocolombium	8.9×10^{-4}	1.6×10^{-3}	UA	UA
Ferrophosphorous	8.0×10^{-2}	1.2×10^{-1}	UA	UA
Silicomanganese	1.7×10^{-1}	1.9×10^{-1}	1.2	1.3

Manganese and chromium, at 26 and 10 million tons per year of world production, respectively, are second and fourth in the world's most needed and used metals. A significant fraction of each of them is produced electrolytically. They are found in large quantities in fine electrostatically collected dusts from other processes, and 98 percent of the manganese and 91 percent of the chromium used in the United States is imported. Therefore, these metals meet the criterion of high consumption rates, require electrical energy for their production, appear as fine dust in the scrap recycle loop, and are fifth and eighth in the list of strategic metals in Table 4-3. Since they also have a relatively high mark-up value between the ore and the usable metal, they are strong candidates to economically support the development of large-scale plasma processing equipment with an expected reasonable return on investment. Because these metals are largely used in ferroalloys they, along with ferrocolumbium, ferrosilicon, and ferromolybdenum, constitute a class of materials that show the greatest opportunity and economic incentive for plasma processing development (Table 4-2).

Zinc also meets many of the criteria listed for plasma processing applications. At 6.5 million tons per year of world production, it is the sixth most important metal. A large fraction of zinc is produced electrolytically, appears in baghouse dusts therefore meeting the recycling criteria, and is the twelfth most important strategic metal as 60 percent of U.S. requirement is imported (Table 4-3). Research has been carried on through pilot-demonstration scale of zinc smelting from primary raw materials by plasma technology as well as the recovery of zinc from waste dust [16,24].

Nickel is eighth in world level of production; some of it is produced electrolytically, and since 73 percent is imported it is the tenth most important strategic metal. Cobalt (usually associated with nickel) is, at 93 percent imported, the fifth most important strategic metal. Plasma processes have been developed to the pilot plant stage to recover nickel and cobalt; and zinc, iron, chromium, and molybdenum have been demonstrated to be recoverable from steel-mill baghouse dust using plasma generators [24,25,26].

Aluminum, magnesium, and titanium fall in a group that is primarily produced electrolytically (although magnesium can also be pyrolytically produced by the reduction of calcined dolomite with ferrosilicon in a

TABLE 4-3 U.S. Net Import Reliance for Selected Metals as a Percent of Consumption

Metals	Percentage of Consumption	Major Foreign Sources
Columbium	100	Brazil, Canada, Thailand
Strontium	100	Mexico, Germany, Canada
Manganese	98	South Africa, Gabon, Brazil, France
Bauxite and alumina	94	Jamaica, Australia, Guinea, Surinam
Cobalt	93	Zaire, Belgium-Luxembourg, Zambia, Finland
Chromium	91	South Africa, USSR, Phillipines
Tantalum	90	Turkey, Thailand, Canada, Malaysia, Brazil
Platinum-group metals	88	South Africa, USSR, England
Tin	79	Malaysia, Thailand, Bolivia, Indonesia
Nickel	73	Canada, Norway, Botswana, New Caledonia
Potassium	65	Canada, Israel
Zinc	60	Canada, Mexico, Spain, Germany
Cadmium	55	Canada, Australia, Mexico, Belgium-Luxembourg
Tungsten	33	Canada, Bolivia, China, Thailand
Selenium	52	Canada, Japan, Yugoslavia
Antimony	48	South Africa, Boliva, China, Mexico
Barium	41	Peru, Ireland, Mexico, Morocco
Titanium (ilmenite)	23	Australia, Canada, South Africa
Mercury	28	Spain, Algeria, Italy, Japan
Iron ore	25	Canada, Venezuela, Brazil, Liberia
Iron & steel scrap	37	Net Imports
Gold	18	Canada, USSR, Switzerland
Vanadium	17	South Africa, Chile, Canada
Iron & steel products	15	Japan, Europe, Canada
Copper	14	Chile, Canada, Zambia, Peru
Silver	7	Canada, Mexico, Peru, England

resistively heated slag furnace). Titanium is produced by the reduction of titanium tetrachloride with magnesium metal. These metals, with aluminum at 16 million tons per year, magnesium at 330,000 tons per year, and titanium at 84,000 tons per year, are third, ninth, and eleventh in world production. Aluminum, whose ore bauxite is 94 percent imported, falls into the strategic metals category. In the future, plasma production of both aluminum and magnesium may be possible, but this will require solving two difficult problems, development of a rapid quenching technique and the need to make the process sufficiently energy efficient (heat lost in quenching must be recovered).

In order of likelihood of application these are the production of ferroalloys from recycled fine material coupled with the reduction of lean ores, the recycling of scrap materials such as cast iron chips, and the treatment of waste dusts that are an environmental concern and contain valuable constituents such as zinc, nickel, chromium, and molybdenum. The treatment of recycled materials, waste products, and lean ores could be followed by primary reduction of zinc, titanium and molybdenum with ultimate application to primary reduction of iron, steel, and aluminum. But torches must first reach the 20 to 40-MW level, reaction chambers must be designed with sufficient residence time, and the problems of rapid quench and heat recovery be solved. With a national commitment and proper funding, solutions can be found, perhaps by the year 2000. The application of plasma technology to primary production of metals could be accelerated and brought to fruition before that time, as previously described, if the synergistic relationship between industries could be organized to produce lower capital investment, operating costs, and higher energy efficiency through an integrated industrial complex producing many products and having greatly reduced waste problems.

STATE OF THE ART

At present, plasma reactors for extractive metallurgy are being developed through trial-and-error, with reactor designs varying considerably for different metals and sometimes even for the same metal. Despite the empirical rather than theoretical foundation for equipment design, the technical promise for plasma furnaces in extracting metals from their ores is well established. Even with pilot-scale successes, however, there are no full-scale commercial installations documented in the open literature.

The reason lies with the production size of smelting systems. Plasma torches with the capacity to equal current productivity--i.e., the 20-MW torch in operation at Westinghouse Electric's Waltz Mill, Pa., facility--remain in the development stage and are not yet commercially available [27]. For instance, a modern economic steel smelter must operate at 250,000 tons per year minimum or 28 tons per hour. Producing this quantity of metal from ore requires a plasma furnace of about 100 MW. Although multiple torches could supply this power level, existing equipment does not lend itself readily to tonnage production. Recent advances in transferred arc reactors (in East Germany and the Soviet Union), however, have greatly enhanced this possibility through the evolution of commercial scale plasma furnaces of 10 to 20-MW capacity using multiple plasma torches of 3.0 to 3.5-MW in ferroalloy production and steel processing [1].

Economic success of the mini-mills producing high-alloy steels and ferroalloy from scrap in electric furnaces has shown that electrical energy can be used economically in special metallurgical applications. During the past 20 years considerable bench and pilot scale experience has been acquired, and the successful economic applications of plasma furnaces are increasing rapidly.

Iron and Steel

Research and development on iron and steel have been directed toward three major areas: reduction of finely divided iron oxide to molten metallic iron; plasma torch augmentation of existing blast furnaces to reduce coke requirements; and the use of plasma reformers to produce the reductant gases used in the direct reduction of iron ore (DRI). The latter yields a powdered sponge iron that is produced at a temperature lower than its melting point.

Iron Oxide Reduction

Beginning in 1970, there were numerous laboratory-scale investigations on the reduction of iron oxide particles to metallic iron in plasma reactors [28-32]. In nearly all of this work the particulate ore was injected with reducing gases into the hot plasma, relying on high temperature to cause the reaction to produce molten iron in the very short residence time available, and subsequently showing low yields. A major step in the solution of this problem was made by the Bethlehem Steel Corporation in 1975. This demonstrated the production of molten iron at the 1.0-MW power level by using a falling-film plasma reactor of Bethlehem's design to greatly increase residence time and temperature. More recent research at SKF Steel in Sweden, using a coke-packed column to increase residence time, has also resulted in a design that produces molten iron using a 1.5-MW power level.

Energy and materials balances derived from the data generated in the 1-MW pilot unit showed gross electrical energy requirements to be 3000 kWh/ton of iron. Losses due to equipment cooling water, etc., were included in this figure, but no credit was taken for the carbon monoxide and hydrogen content or the sensible heat of the effluent process gases, which contained an energy equivalent of 685 kWh/ton. In the United States, the projected electrical energy cost of this technically feasible one-step route for making carbon-free molten semisteel from iron ore will not be economical unless some means is developed to use the reducing value of the by-product gas as well as the sensible heat in this gas and in the cooling water.

It is quite possible, however, that new commercial initiatives may be taken regarding the use of plasma technology in the iron and steel industry. As an example, SKF Steel believes the proper combination of conditions already exists for this technology and in diligently pursuing customers for its Plasmasmelt process. Pickands Mather and Company of Cleveland, Ohio, along with the State of Minnesota, has entered into a $3.7 million contract with Westinghouse to develop a plasma reactor for the transformation of Mesabi Range iron ore to molten iron, eliminating the present pelletizing step and upgrading the product before it leaves Minnesota. In December 1983 they announced the anticipated construction of a 100,000-ton-per-year demonstration

plant in 1984-1985, to be followed by an expansion of another 100,000 tons at
a later date if all goes well with the development program [33]. Some
important patents in this area have been granted [34,35,36].

Plasma Augmentation of Blast Furnaces

Environmental constraints on existing coke ovens and the increasing cost
of good-quality metallurgical coke have led to considerable effort to replace
some of the metallurgical coke requirement with other fuels, such as the
introduction of natural gas, coal, or oil at blast furnace tuyeres. The use
of electrical energy from a plasma torch at the tuyeres in a similar manner
may increase blast furnace productivity while reducing coke requirements.
This idea has been successfully demonstrated at the Centre de Recherches
Metallurgiques (CRM) in Belgium, where superheated reducing gas produced by
the plasma reforming of natural gas with air or carbon dioxide was injected
into a pilot blast furnace, resulting in a 75 percent reduction in coke
consumption [16,37]. Technically feasible, the augmentation of hot blast
energy by plasma torches may or may not be economically attractive, depending
on the local circumstances.

Direct Reduced Iron Via Plasma Reformers

SKF steel has demonstrated the technical feasibility of plasma cracking of
natural gas or liquefied petroleum gas (LPG) to an acceptable reducing gas
mixture for producing sponge iron. The current operating capacity is 70,000
tons of sponge per year.

ASEA, located in Vasteras, Sweden, has developed a dc plasma arc furnace
to replace conventional arc furnaces for melting scrap. The original
objectives were to treat fines without agglomeration, decrease electrode
consumption and decrease electrical arc noise, but the firm is now extending
its application to the chemical reactions of extractive metallurgy. This
furnace is a basic element in the Elred process involving the fluidized bed
prereduction and plasma smelting of iron ores [16,38,39]. The Elred process
consists of three basic processing steps:

1. The prereduction of finely divided iron ore carried out in the solid
    state in the presence of excess carbon to produce a partly metallized
    carbon-containing product;

2. Plasma smelting of this product to molten iron;

3. The generation of electrical energy using the off-gases from both the
    prereduction and plasma arc furnaces in a combined-cycle cogeneration
    system.

The final step produces all of the electrical energy required for the plasma
arc while generating 300 to 400 kWh/ton of steel as a by-product. Energy
consumption does not differ significantly from large blast furnaces, but
capital investment is significantly lower and the use of coal instead of coke
as the energy raw material results in substantially lower energy cost.

By replacing the natural gas heating fuel with hydroelectric power via plasma torches, Sidebeck-Dosco Ltd., Montreal, a steelmaker that uses DRI, is investigating the possibility of reducing operating costs in its methane reformer at its DRI operations at Contrecoer, Quebec. The module under consideration for conversion has a capacity of 500,000 metric tons of DRI per year but would be increased to 550,000 metric tons by the conversion. Natural gas is currently used as fuel to heat the reformer segment as well as for the production of the reduced product gases. Plasma can be used to replace that portion of the gas used for fuel and is being considered because of the uncertain future costs of natural gas and oil. Sidbeck-Dosco's direct reduction plant is located in an area where hydro-electric power is available and the price is considered to be more stable [40].

Ferroalloys

One of the most active areas in the application of plasma technology to extractive metallurgy is the production of specialty ferroalloys. The present method is to melt recycled scrap and DRI with further reduction in conventional submerged arc furnaces to produce specialty steel products.

The first large scale comparison of plasma with conventional technology was recently reported based on the operation of a 10-ton per hour plasma furnace operating since 1973 and a 30-ton per hour furnace in operation since 1977, both in the German Democratic Republic [41].

Advantages of 30 percent lower capital investment than a modern high-powered electric arc furnace, less than 2 percent iron loss, and low oxygen and hydrogen contamination were reported. Higher melting efficiency with no need for secondary refining, greater recovery of alloying elements in scrap, lower noise levels (below 60 decibels), and the ability to produce low carbon alloys and alloys with nitrogen through the gas phase instead of expensive ferroalloys were reported. This, coupled with the elimination of shock loading of transmission lines and production of a higher quality product indicates significant advantages over conventional submerged arc furnaces.

Similar results are reported from furnaces with six 3.5-MW torches having capacities of 100 tons of steel per hour reported to be operating in the Soviet Union. These furnaces produce both ferroalloy and hot metal, using DRI and scrap as the charge [1].

The most extensive investigation in the possible commercialization of plasma furnaces for ferroalloy production in the free world is being conducted by the Council for Mineral Technology (MINTEX) in South Africa in conjunction with the Middelburg Steel and Alloys Company (MS&A). Their experiments were conducted at the Tetronics Research and Development Company Ltd., Faringdon, Oxon, England, using the Tetronics Plasma System (TPS) with a 1.4-MW transferred arc furnace and a precessing cathodic electrode and liquid metal anode [16]. Experiments have been conducted on the production of both ferromanganese and ferrochromium [42,43]. Chromium recoveries as high as 98 percent were obtained in the production of high-carbon ferrochromium from a Transvaal chromite ore (chromium-to-iron ratio of 1.7:1) and powdered coal at 750-kW power input. The precessing electrode serves to expand the plasma

zone. The powdered feed, consisting of a mixture of ore, coal, and additives for slag treatment, is injected into this zone. Since conventional submerged-arc furnaces producing ferrochromium typically operate at above 3800 kWh per metric ton, about equivalent to the 3500 to 4000 kWh per metric ton reported for these experiments. It seems likely, therefore, that the plasma was simply a convenient, efficient heat source for the reduction of dissolved ore in slag with a conventional liquid metal bath and that little in-flight reduction took place, even though the arc was expanded. Precession of the electrode may be necessary to aid heat transfer and hold reactants at temperature, but it is unlikely that arc expansion can provide the necessary residence time for in-flight reaction, as has been suggested [44].

Increased efficiency would be obtained by prereduction of the ore, which could result in low energy consumption of the order of 2000 kWh per metric ton and produce more favorable chromium-to-iron ratio alloy from low grade ores [45,46]. Elimination of the agglomerating plant, the use of low-cost coal powder instead of coke or char, high chromium recoveries, and lower electrode costs should result in significant cost savings, even though energy requirements are equivalent to existing submerged arc processes. Reduction of operating costs on the order of 20 to 30 percent have been predicted [47].

SKF Steel's Plasmasmelt process using nontransferred plasma arc torches at the base of a coke-filled column has also been demonstrated successfully in the production of ferroalloys [48]. Ferrochromium has been made from ore fines or concentrates and the process is available for license under the trade name of Plasmachrome. Other ferroalloys can also be made in this processing equipment, and licensing for ferroalloys other than ferrochromium is marketed under the trade name Plasmalloy.

The Bethlehem Steel falling-film reactor has also been applied to the production of ferrovanadium [49]. Tests were conducted on a 500-kW facility capable of producing up to 2 million pounds per year, and at this level it could be considered to be a production unit. Reaction rates were 10 to 15 times greater in the falling-film plasma region and in the bath than in-flight, and the carbothermic reduction of the oxide could be considered to be nearly complete by the time it reached the pool. The alloy contained 43 percent vanadium at about 80 percent vanadium efficiency and an overall efficiency of 72 percent of the metallic fraction of the ore. Energy consumption was approximately 3000 kWh per metric ton of alloy, with net energy consumption close to the theoretical limit when calculated heat losses were subtracted. Both the ferrovanadium and pure vanadium made with this process were tested as additives for steel and found to be satisfactory. Although no direct cost estimate has been published, estimates can be made using data from related processes. Assuming a power of 560 kW, a production rate of 450 metric tons per year, and energy consumption of 220 GJ per metric ton, showing a near stand-off with present production costs and yields a 1.5 percent improvement with the best possible estimates [14]. Commercial 80 percent ferrovanadium (analyzing 79.4 percent V, 18 percent Fe) has also been easily produced in the Hydro-Quebec-Noranda plasma furnace by reacting vanadium pentoxide with iron and carbon [1].

Waste Materials and Zinc

Each year industry generates large quantities of waste dust that must be discarded in safe landfills at considerable cost. By far the largest single contributor to this particulate waste is the power generating industry, which produces over 120 million tons of fly ash each year. Other sources of such dust are open-hearth steel furnaces, basic oxygen furnaces, and electric arc furnaces of various types. Many of these dusts are hazardous and must be encapsulated or transported to a controlled landfill because of the possible leaching of toxic heavy metals such as lead, cadmium, and chromium. Because much of this material has been condensed from the gaseous state at very high temperatures, it is finely divided, ranging from 0.1 μm to 1.0 μm and is of a glassy nature and each particle may contain more than one metallic constituent. This makes normal techniques of ore concentration, such as flotation, not feasible.

In examining these in some detail, between 1 and 2 percent of the charge to an electric furnace is collected as dust in precipitators or baghouses and may contain as much as 25 percent zinc, 4 percent lead, and 2 percent manganese as oxide, if carbon steel using some galvanized scrap is being processed [25]. If the furnace is located in an alloy steel plant, the waste dust may contain 25 percent chromium oxide, 19 percent manganese oxide, 5 percent nickel oxide and some molybdenum oxide [25]. In both cases the iron content is between 20 and 30 percent, whereas blast furnace dust and basic oxygen furnace dust and mill scale contain about 50 percent iron and 1 percent manganese oxide. Of these recoverable metals, the United States imports 98 percent of the manganese, 91 percent of the chromium, 60 percent of the zinc and 25 percent of the iron needed for its industries. As early as 1977 it was suggested by workers at the University of Toronto's Department of Metallurgy and Materials Science that a high temperature plasma arc process may be applicable to resource recovery from steel plant dust [25]. Research was carried out in a furnace of their own design in which an arc is struck between three hollow graphite electrodes, using 3-phase alternating current. Their results from the treatment of steel plant waste powders mixed with stoichiometric carbonaceous material and fed continuously into the reactor showed the successful production of molten iron and ferroalloys and an overhead condensate of zinc and lead, which was easily recovered. Their economic projection suggested that such operations could be economical, even on a small scale.

More recently, SKF Steel of Sweden demonstrated the feasibility of metal recovery from such fine dust in a plasma process at the 1.5-MW pilot scale using a modification of their Plasmasmelt equipment, termed the Plasmadust process. In this process fossil energy in the form of carbon monoxide and hydrogen is retained as the reductant, but the thermal energy is provided by a plasma torch operating at 85 to 90 percent electrical energy efficiency, resulting in a much-reduced gas volume over conventional fossil based processes. Because of the high enthalpy of the plasma gas, capital investment in the equipment is significantly reduced while total energy efficiency is much improved. SKF now has units of 3 and 6 megawatts available and is working on a 10-MW system it believes will be the largest module necessary for the development of extractive metallurgical plasma systems [26].

A new company called Scandust has been formed by SKF, Landskrona, Finans, and the Swedish government to recover metals such as zinc, iron, nickel, chromium, and molybdenum from steel-mill baghouse dust based on the plasmadust technology. A 70,000-ton per year plant is under construction at the Oresund Shipyard in Landskrona, Sweden, at a cost of $26 million and is expected to be in full operation by the end of 1985 [24].

Only slight modifications are needed to convert the Plasmadust process to the production of pure zinc from its ores. This process has been demonstrated at the 1.5-MW level and licensing is being marketed under the trade name of Plasmazinc [26].

Zirconium, Silicon, and Titanium

Zirconium, silicon and titanium may be grouped together, since the present process used for the production of both titanium and zirconium involves the reduction of the chloride with magnesium (Kroll process). Titanium and zirconium metal sponge are produced, and the magnesium chloride by-product is recycled through an electrolytic process to regenerate the magnesium and chlorine for both the chlorination and reduction steps. Although commercial-grade silicon is readily made in submerged arc furnaces, the impurities remaining in the silicon render it unusable for solar cells, which are expected to be a significant new market for this metal.

Zirconium

Since early 1981 researchers at both the Industrial Materials Research Institute (IMRI) in Boucherville, Quebec, and at McGill University in Montreal have been developing a plasma process using the Hydro-Quebec-Noranda transferred arc reactor [1] to replace the high-cost conventional Kroll process for the production of zirconium. The production of the chloride is no problem since technology for the plasma decomposition of low cost abundant zircon sand ($ZrSiO_4$, Zirconium silicate) to yield relatively pure zirconium dioxide has been in commercial operation for a number of years at Ionarc in Bow, New Hampshire. The chlorination of metal oxides in fluid beds used in commercial production of titanium tetrachloride for the Kroll process and has been demonstrated by Alcoa on pilot- and demonstration-plant scale for the production of aluminum chloride for the Alcoa Smelting Process (ASP).

The McGill group also investigated the production of zirconium tetrachloride in a chlorine plasma by the chlorination of zirconium dioxide, both with and without carbon additions. At 1700 K, chlorination readily occurred, but the reaction was significantly faster in the presence of carbon.

With commercial techniques for the production of zirconium tetrachloride from zircon sand, the proposed plasma process for the production of zirconium metal seems both technically and economically feasible, showing a calculated cost of production of dense zirconium metal at $4-5 per kilogram (1983 dollars) if the removal of hafnium is not necessary.

Silicon

In the years between 1973, when the oil crisis first began, and 1979, many thought that solar energy might play a very significant role in the country's needs for electrical energy if the price of photovoltaic-grade silicon could be reduced. The Department of Energy scenarios projected a market of 3000 metric tons per year by 1985, far exceeding existing capacity [14]. Although many now believe the role of solar power production will be much less important than previously thought, there should be a definite place for this form of power generation, and a modest program continues. Westinghouse Electric suggested a one-stage high-temperature plasma process, which was successfully carried up through the 1.5-MW pilot plant stage [7,14,38]. A very high temperature is used in this process, permitting liquid silicon to be condensed onto the furnace wall protected by a frozen skull and collected as a liquid at the bottom of the unit. The silicon is made by the reaction of gaseous silicon tetrachloride with metallic sodium in an argon-hydrogen plasma, producing pure silicon and sodium chloride. The sodium chloride is removed as a vapor, condensed and recycled. Using data from the 1.5-MW pilot plant, economic analysis of a projected 3000 metric ton per year plasma silicon plant showed a $25 million capital requirement and an estimated product cost of $13 per kilogram in 1980 dollars. This was clearly in line with the Department of Energy's goals, out uncertainty as to the size of the market caused shelving of the process development for strategic rather than technical reasons.

Work continues in many areas at a somewhat reduced level aimed at the low cost production of photovoltaic silicon, and a paper was recently presented at the Sixth International Symposium on Plasma Chemistry in Montreal, describing a plasma process for multiphase zone refining that shows tremendous economic advantage over the classical zone melting technique.

Titanium

Its relatively low density, corrosion resistance, and high strength make titanium very attractive for use in the aerospace industry as well as in chemical and power plants. Titanium use has, however, been restricted by its high cost, except in the aircraft industry where cost is of somewhat lesser importance. The high cost results largely from costly fabrication techniques and high recycle loads but is also heavily influenced by the batch nature and high energy consumption of the conventional Kroll and Hunter smelting processes. Plasma application in the production of titanium metal has received periodic attention over the past 30 years, most cases being concentrated on hydrogen reduction of titanium tetrachloride, thereby retaining the first two steps in the Kroll or Hunter processes. Over the years many attempts were made to produce titanium powders for metal by this route with little success, since only partial reduction was attained and a mixture of titanium subchlorides were the usual product [50-51]. In 1974, Yean and Riter [52] concluded that extremely rapid preferential condensation of vapor-phase titanium would be necessary if the unfavorable thermodynamics of the system were to be overcome. In 1972 a British patent was issued suggesting that the traditional Kroll or Hunter reduction using sodium or magnesium be carried out at plasma temperatures to directly produce

high-purity titanium and result in the elimination of the subsequent
purification. Depending on processing conditions, titanium alloy powders,
pure titanium powder, a form of ingot cast from the liquid state, or a
substitute for sponge could be produced. For a number of years, the
Electricity Council Research Center in Chester, England, has been
investigating a single-stage gas-phase reduction of titanium chloride with
sodium in a hydrogen plasma at 2300 K [53]. Researchers have successfully
prepared metallic titanium in a 30-kW plasma furnace and have shown it to be
substantially free of chlorides. However, considerable difficulty has been
experienced in controlling the addition of the feed materials [1,54].
Following the same idea and using techniques p. .viously developed for the
production of photovoltaic-grade silicon, Westinghouse Electric has
successfully demonstrated the production of titanium metal in various forms
using a 40 kW laboratory unit. The sodium chloride by-product is removed as a
vapor, permitting continuous operation. Data collected from this unit have
been used in designing a pilot scale reactor, the information from which could
be used to scale up to a production unit [55].

CONCLUSIONS AND RECOMMENDATIONS

With few exceptions, the application of high-temperature plasma reactors
to extractive metallurgy is still unde · laboratory or pilot-plant
development. Various plasma phenomena have been recognized since 1790 and
used commercially since the turn of the century, when large-scale electrical
generating equipment became available. Exploitation, however, has been rather
crude, found largely in inefficient, noisy, and polluting arc furnaces used
only where very high temperatures are needed to produce materials that command
a high price. Relatively large-scale plasma equipment did not become
available for metallurgical applications until NASA found it necessary to
develop efficient torches for the investigation of reentry materials. At that
time there was a great rush to apply plasma technology to the development of
new products and processes, using hardware already developed. This bypassed
the fundamental studies that could have led to efficient design. In the past
10 years, however, bench and pilot scale experiments have made possible the
application of plasma technology to bulk metal heating and melting and as a
heat source for fluidized beds and rotary kilns. Plasma technology has also
been used as a supplement for blast furnaces and in a few instances for
high-temperature chemical reactions.

In recent years, a number of important extractive process applications
operating at power levels up to 20-MW using multiples of 3 to 5-MW torches
have been brought on stream or are in advanced stages of development:

- Plasma arc melting: Remelting of high alloy steels under inert
  atmosphere permits the alloying of reactive metals without
  oxidation. Applications of this type have been in operation since
  the early 1970's.

- Production of ferroalloys: Manganese, chromium, vanadium, columbium,
  silicon and other materials needed for alloying with steel are
  produced in the form of ferromaster alloys from lean ore fines,
  concentrates, and scrap materials. Some time ago, the technical

feasibility of such production was demonstrated at the 400-kW level, but commercial exploitation was delayed until 10 to 20-MW assemblies were available.

- Recovery of metals from precipitator dusts: A 70,000-ton-per-year plant, to be completed in 1985, at a cost of $26 million, is under construction in Landskrona, Sweden.

- Blast furnace augmentation: Air blasts, superheating, and fuel injecting systems (designed to increase productivity) are under development.

- Other processes: Technologies developed beyond pilot scale but not yet commercialized are: (a) smelting of zinc from primary raw materials, (b) direct reduction of iron ore with hydrogen or methane, and (c) hot metal from iron ore concentrates and coal.

Once a technology has been developed, it is usually more economical to purchase the proprietary technology from the developer than to try to produce similar results at a lower cost through independent investigations. Therefore, it seems that, since many of the processes described here have been offered for license, it would waste research funds to develop competing processes to accomplish the same result with similar technology. Instead, since little is known of the fundamental nature of plasma interactions, it would be better to invest the available funding in the basic research needed to close the gap between the fundamentals of plasma arc phenomena and the physics and chemistry of process metallurgy. The required research can be broadly divided into three parts and conducted under three auspices.

The fundamental research and mathematical modeling of high-temperature reactions in the plasma should be carried out at universities or national laboratories, where research can be targeted to yield mathematical models based on theory as well as empirical observation describing heat, fluid flow, and transport phenomena under plasma conditions. Other fundamental investigations to determine thermodynamic properties and transport coefficients under plasma conditions will also be necessary. Diagnostic techniques must be developed to define the size, injection velocity, and temperature profile of particles entering the reaction zone.

Industrial laboratory investigations should focus on such engineering factors as designing systems with the required residence times prescribed by the fundamental investigations as well as the practical problems of material selection. Important materials considerations include avoiding refractory erosion and electrode wear, arc control, hearth erosion, and means for recovering heat.

Economic analysis is separate from the scientific and engineering evaluation. For capital investment to be warranted the finished product must have a market sufficiently large and at a high enough profit to give a proper return on investment. The likelihood of meeting this requirement can only be determined by an in-depth economic study of proposed applications, which will assist in selecting processes for development that will be commercially as well as technically successful.

In summary, if plasma technology is to find a place in United States extractive metallurgy processes, a long range program must begin with fundamental studies of the plasma process as it relates to the needs of extractive process metallurgy and progress through the engineering development of new techniques needed for metal separation. Two or three centers should be created at universities, and possibly national laboratories or other research organizations, with complimentary and supplementary activities directed toward sufficient understanding of plasma reactors to develop design criteria for virtually any physical or chemical separation. This requires equipping these centers with basic equipment, and should be a joint government-academia-industry undertaking to put American industry on the track to restoring our world leadership in basic extractive metallurgy technology.

American industry will always be willing to finance the development costs of new products and processes in the short time frame and the National Science Foundation, coupled with academia, has been available to fund the basic research necessary. We are weakest in the 10-15 year time frame where uncertainty as to whether the research will pay off causes industry to look twice at funding research and development on new production processes or to rejuvenate old techniques. The government has been reluctant to fund this type of research, deeming it the proper province of industry. This has not been the case with our foreign competitors, who, if we exclude military R&D, are substantially outspending us on civilian research and development. This is beginning to pay off for them, and if we do not find some way to increase civilian research and development in extractive metallurgy in the United States we will not be competitive in international markets.

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Chapter 5

PLASMA DEPOSITION PROCESSING

More than any other application for plasmas discussed in this report, plasma deposition is an established industrial process. However, the practice has developed empirically, and the science base is in its infancy.

Among the most well-developed and widely-used plasma deposition processes are those that employ high-intensity plasma flames for melting and consolidating pre-alloyed powder feed onto the workpiece surface. These processes can be conveniently classified into three categories: conventional plasma spraying, vacuum plasma spraying, and plasma transferred arc deposition. This chapter describes essential features of these three processes, their strengths and limitations, and their areas of application. Processing fundamentals are also considered, particularly as they relate to particle/plasma (melting) and droplet/substrate (solidification) interactions, since this is the key to process optimization. In addition, a background of plasma-arc jet theory, and development of plasma spray deposition methods is presented [1-3]. Most of the literature reviewed will deal with conventional plasma spraying at relatively low jet velocities and atmospheric pressure.

PROCESS DESCRIPTION, EQUIPMENT, AND APPLICATIONS

Process Description

Plasma spray deposition, or "plasma spraying," is a process that combines particle melting, quenching and consolidation in a single operation. The process involves injection of powder particles (metallic, ceramic or mixed powders) into a plasma jet stream created by heating an inert gas in an electric arc confined within a water-cooled nozzle. The particles injected into the plasma jet (temperatures approximately 10,000 K and higher) undergo rapid melting and at the same time are accelerated toward the workpiece surface. Rapid quenching of the molten particles occurs when the droplets impact on the substrate. Cooling rates are typically 10^5 to 10^6 K/sec, and the resulting microstructures are fine-grained (~ 0.5 μm) and homogeneous.

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Conventional plasma spraying (CPS) is normally carried out at atmospheric pressure. Typically, the deposits contain oxidation products, together with some porosity due to incomplete melting, wetting, or fusing of deposited particles. The problem of oxidation can be minimized by "shielding" the plasma arc with an inert gas atmosphere. An alternative approach is to enclose the entire plasma spraying unit in an evacuated chamber, which is maintained at about 30 to 60 torr inert gas pressure by high-speed pumping. Under these conditions of "vacuum plasma spraying" (VPS), gas velocities are much higher (typically in the Mach 2 to 3 range), because of the higher permissible pressure ratios. Other advantages of VPS, compared with CPS, include higher particle velocities, which produce denser deposits (often > 98 percent of theoretical density), broad spray patterns, which produce large areas of relatively uniform deposition, and transferred arc heating of the substrate, which improves deposition characteristics. In addition, the VPS process can be automatically regulated to make controlled deposits on complex geometries at reasonably high deposition rates (up to 50 kg per hour).

Plasma transferred arc deposition is essentially a weld overlay process in which the source of alloying material is a continuous powder feed. Normally, the plasma jet heats the substrate to the point where some surface melting occurs. This is an important feature of the process, since it is the means by which a good metallurgical bond is achieved between weld overlay and substrate. Great care, however, needs to be exercised to avoid excessive melting of the substrate, since, by an alloy "dilution" effect, this could seriously impair the quality of the overlay coating.

Until recently, transferred arc technology had been applied almost exclusively to weld overlay processing. With the advent of VPS, however, and the effect of the low pressure environment in diffusing the transferred arc, it has now become possible to combine VPS and transferred arc technologies. In this new hybrid system, the transferred arc can be either polarity: workpiece (+) for heating, and workpiece (-) for substrate cleaning. Workpiece heating occurs via joule-type heating, whereas cleaning is believed to occur via vaporization of thin oxide films from cathodic arc spots caused by a field emission effect.

Processing Equipment

Equipment requirements for plasma spraying include a plasma jet generator, (typically) dc rectifiers, water cooling/heat exchanger/pump circuit, powder feeders, gas supplies, and a control console with switches and meters for power, gas, and water control. In addition to these basic needs, auxiliary equipment might include ventilation spray booths, acoustic protection, radiation protection (infrared and ultraviolet), manipulation devices for gas and/or substrates, and potentially even interactive controls. When spraying using a shroud, a gas supply and method of injection are required, and when spraying in a controlled environment chamber a water-cooled enclosure is necessary.

The typical design of a modern plasma spray gun (Figure 5-1), incorporates a conical thoriated tungsten cathode (the tip is usually molten for enhanced thermionic emission), a water-cooled copper anode (nozzle), a gas injection system, and a powder feed device. Gases employed in such a design are
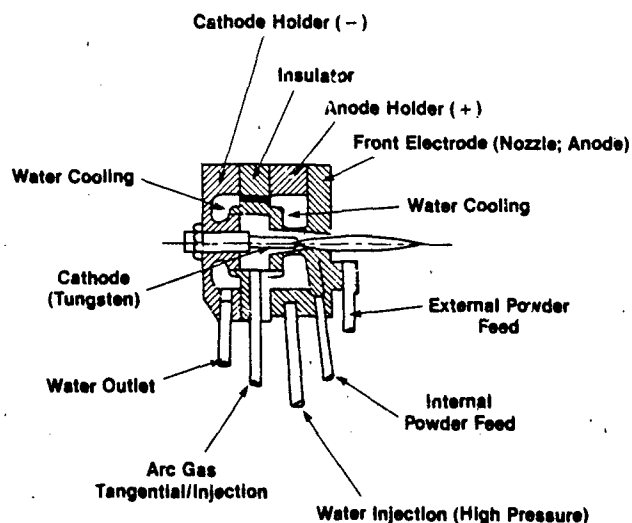
FIGURE 5-1 Schematic of typical plasma spray gun.

selected for inertness and/or energy content (Ar, Ar/He, Ar/H$_2$, N$_2$ and N$_2$/H$_2$), and are injected axially, or tangetially behind the cathode (Figure 5-2); tangential injection achieves vortex stabilization of the plasma flame.

Historically, power levels and nozzle designs have been one of the major areas of development. Early gun designs operated in the 5 to 10 kW range at subsonic plasma jet exit velocities. As nozzle cooling technology developed, power levels increased to the 30 to 40 kW range, and jet exit velocities became supersonic. Recently, further increases in jet exit velocities have been achieved by incorporating the plasma gun in a reduced pressure chamber. Some guns in VPS systems now deliver 80 to 120 kW, with jet exit velocities exceeding Mach 3. Nozzles have also been modified for better cooling, higher expansion ratios, and in some cases longer throat lengths. It has been proposed that a longer throat lessens radial temperature (and enthalpy) gradients and increases heat transfer to the powder particles.

Efficient powder injection for optimum melting has been another area of continuing development. Because of the complexity of the problem, due to the high thermal and velocity gradients in a typical plasma jet (Figure 5-3), optimal designs have been realized largely by empirical methods. In most systems, powder injection ports are located either within the nozzle (anode), or downstream of the nozzle, depending primarily on the characteristics of the plasma gun and on the type of powder being sprayed. An additional complication is the need to provide adequate protection against environmental interactions after particle melting has been achieved. This is usually accomplished by injecting a shroud of inert gas around the periphery of the jet and/or around the substrate. In the VPS system, the reduced inert-gas pressure environment provides the needed protection. Using such techniques to minimize environmental interactions, high quality, metallurgically sound

Cathode   Nozzle Anode   Gas Tangential Injection

a) Arc Plasma Torch Stabilized By Eddy Gaseous Flow

Cathode   Gaseous Longitudinal Flow

Insulator   Cylindric Channel

b) Arc Plasma Torch Stabilized By Longitudinal Gas Flow
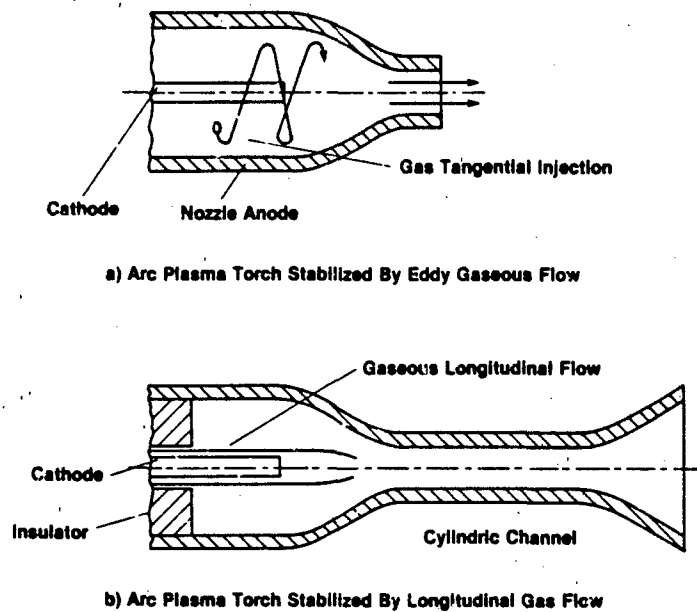
FIGURE 5-2   Principles of dc plasma torch stabilization.

Nozzle Wall   Arc Gas Flow (Spiral)   Partially Melted
Arc Boundary   Fully Melted
Molecule Recombination Zone   Fully Melted & Super Heated
Ion Recombination Zone   Fully Melted
   Partially Melted
Ion Recombination Zone
Powder Feed Tube
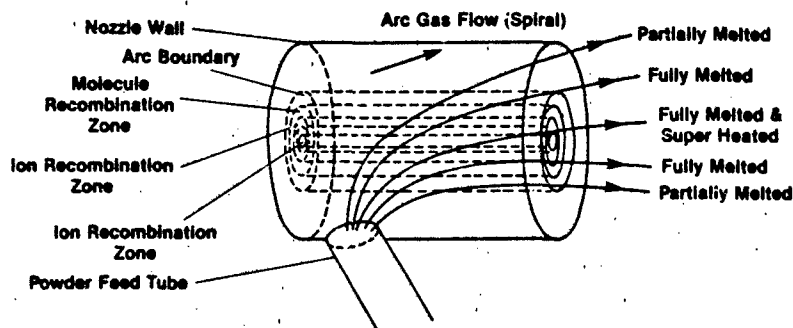
FIGURE 5-3   Thermal gradients through the cross-section of a typical arc jet.

deposits, that are well-bonded to the substrate are routinely produced by plasma spraying, but the best deposits are achieved by the VPS process.

Equipment requirements for transferred ar ocessing are similar in many respects to those needed for plasma spraying. .he basic requirements include a specially designed plasma torch, powder feed and gas delivery systems, control consoles, and workpiece mani lation devices. In addition, in

transferred arc systems, some provision is usually made for first initiating the plasma jet in a nontransferred mode and then subsequently transferring it to the workpiece surface. In a typical design (Figure 5-4), this is accomplished by striking a high-frequency spark between the tungsten electrode (cathode) and the tip of the torch nozzle (anode). The transferred arc is established subsequently by completing the dc circuit between the tungsten electrode (cathode) and the workpiece (anode).
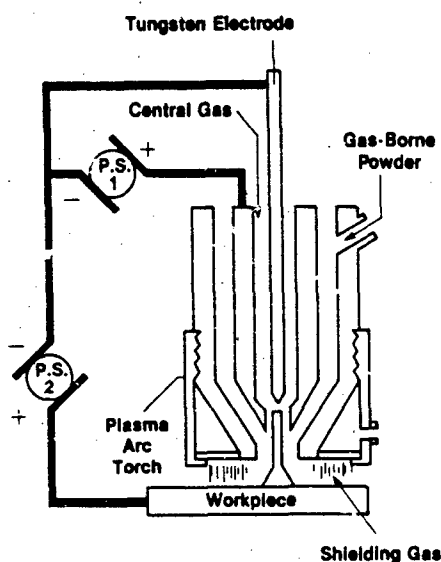
FIGURE 5-4   Plasma transferred arc gun, and deposition process.

In most systems, powders are metered into the plasma column using an inert carrier gas, such as Ar or He. This can be done either within the torch itself (Figure 5-4), or outside of the torch. Low melting point metallic, powders melt almost instanteously in the plasma flame and, at a sufficiently high deposition rate, form into a continuous weld overlay. On the other hand, high melting point powders may not be fully melted when they reach the weld pool, or may not melt at all. In advanced dual-feed systems, this feature is exploited to fabricate composite structures, e.g., refractory carbide dispersion strengthened alloys. Experience has demonstrated that when appropriate shielding gases are used to protect the weld pool from oxidation attack, deposits are fully dense and metallurgically bonded to the substrate.

Applications

Plasma sprayed deposits typically have fine microstructures and contain varying amounts of retained porosity and inclusions, depending sensitively on deposition parameters such as power level, arc gas composition, jet transport properties, and particularly environment. Figure 5-5 compares the microstructures of deposits prepared under three different types of

environment. Without the benefit of a protective atmo. here as in Figure
5-5(a), the deposit contains many large oxide inclusions and a hit density of
pores. With a protective atmosphere as in Figure 5-5(b), both the numbers of
inclusions and of pores are sharply reduced. However, best results are
achieved under conditions of vacuum plasma spraying as shown in Figure
5-5(c). A typical VPS deposit has few inclusions, and the deposit density is
about 98 percent of theoretical density.

<div align="center">(a) Air Spraying   (b) Argon Shrouded   (c) Vacuum Spraying</div>
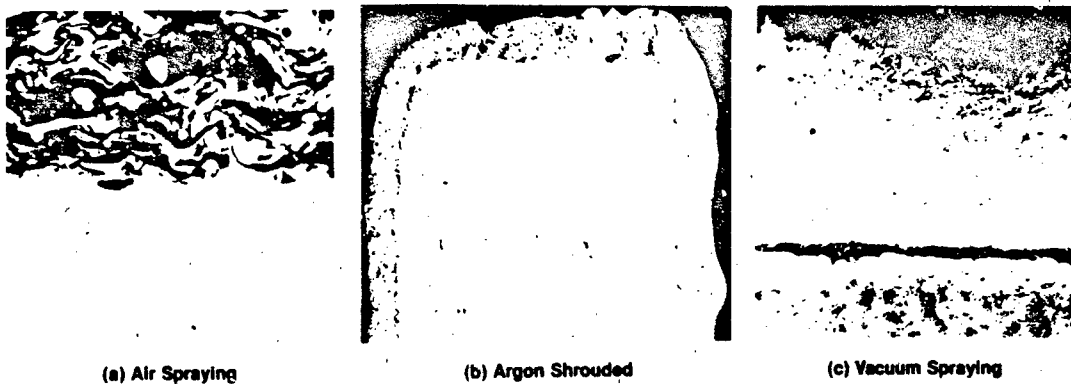
FIGURE 5-5 Co/Cr/Al/Y deposits made by various plasma spraying processes.

Plasma sprayed deposits have been used as protective coatings in corrosion
and wear applications and as high-thermal-flux barriers. Deposits have also
been used for building up worn bearing surfaces, and for making freestanding
relatively thin-walled structures, such as refractory rocket nozzles and
ceramic bodies. More recently, with the advent of VPS, quality coatings of
high performance materials have become available, that are already finding
applications in industrial gas turbines and jet engines. Moreover, given the
metallurgical quality of VPS deposits and the ability to controllably lay down
the material at temperatures over 700 K, it is now possible to build up thick
(> 5 cm) deposits without sacrificing quality. Some experimental components
have already been produced by this means.

Many types of deposits have been produced by conventional plasma spraying,
including refractory metals (W, Ta, Mo), carbides (Cr_3C_2, WC, TaC),
borides (TiB_2, ZrB_2), oxides (Al_2O_3, Y_2O_3, TiO_2), intermetallics
(Cr_3Si_2, $MoSi_2$), and mixed phases (Y_2O_3/ZrO_2, WC/Co). In
addition, special powders have been developed for the purpose of improving the
bond strength between deposit and substrate, e.g., self-fluxing B-rich Co- and
Ni-base alloy powders, and Ni + Al composite powders that experience a strong
exothermic reaction upon melting in the plasma flame. The introduction of
vacuum plasma spraying has further extended the list of sprayable materials.
Thus, advanced coatings of the MCrAlY type (M = Ni, Co, Fe, Ni/Co) and
high-performance Ni- and Co-base superalloys can now be successfully
spray-deposited. Significant increases in the strengths of superalloys have

been achieved by VPS, which have be... attributed to grain ...ize refinement,
microstructural homogeneity, and solubility of solid solution strengtheners.
Dramatic improvements in thermal fatigue performance have also been found in
VPS superalloys compared to as cast material.

Microstructures of MCrAlY and Ni-base superalloy VPS deposits are shown in
Figure 5-6. The structures are homogeneous and contain extremely fine
precipitates. Grain sizes have been measured by TEM and are 0.25 µm or finer
in the regions that have been completely melted and resolidified. A small
fraction of unmelted original powder particles, which have become entrapped in
the deposit, can be noted in the microstructures. However, due to the small
size of these particles (usually < 50 µm) a post-deposition solution anneal
completely homogenizes the structure. It is because of this rapidly
solidified, extremely fine-grained, homogeneous microstructure that the VPS
process is attractive. The process has the potential, in one step, of rapidly
solidifying and consolidating metal particles to make a structurally sound
component.

(a)   (b)

FIGURE 5-6   Vacuum plasma sprayed deposits of (a) Co-29(-)Cr-6Al-1Y coating,
                and (b) Ni-Base superalloy, IN-738.

Plasma transferred arc deposits are produced in a single pass, with
careful control of substrate melting and deposited powder. The optimal
microstructure exhibits minimal melting of the substrate and epitaxial
resolidification of the overlay deposit. The process has been widely used as
a hardfacing treatment for many years, and new applications continue to be
found. The range of applications may be increasing because of the ability now
to create novel composite microstructure by making use of mixed powder feeds.
An example is shown in Figure 5-7, where the Co-Cr-W alloy matrix has been
dispersion strengthened by a high-volume fraction of TiC particles. Such a
microstructure is of interest in abrasive-wear applications.

STATUS OF SCIENCE BASE

The production of dense high-strength plasma sprayed deposits requires
that: (a) a large fraction of the injected powder particles be heated to a
molten state before they impinge on the substrate or the previously deposited

0.4 mm

5μm

(a)   (b)
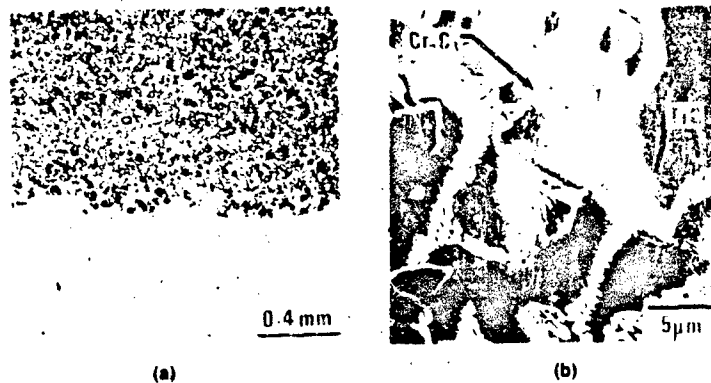
FIGURE 5-7   Plasma transferred arc deposit of TiC dispersion strengthened
              Co-Cr-W: (a) low magnification micrograph of as-deposited
              material showing uniform dispersion of TiC particles; (b) higher
              magnification micrograph showing eutectic carbide in the Co-Cr-W
              matrix.

particles; (b) the particles also have sufficient velocity so as to spread
out and flow into the irregularities of the previously deposited layer; and
(c) a strong interparticle or particle/substrate bond be formed.
Thus a knowledge of the particle/plasma (melting) and particle/substrate
(solidification) interactions during plasma spraying is the key to the
fundamental understanding of the process as well as for process optimization.
Melting and solidification (including spreading and adhesion) phenomena during
plasma-arc spraying are critical to the control of the properties of the
deposit. Most of the science base that is available in the literature (>95
percent) deals with conventional plasma spraying, which takes place at
relatively low jet velocities and ambient pressure spraying conditions. Much
work is needed to understand the fundamental issues in vacuum plasma spraying.

Plasma Arc/Jet Theory

     The electric arc used to produce the plasma is a complex physical
phenomenon that has been described or modeled by many investigators [4-7].
The arc is broken into three major regions (Figure 5-8)--cathode sheath,
positive column, and anode sheath. The positive column represents the true
plasma (charge equilibrium), while the anode and cathode sheath regions have a
negative and a positive space charge with large voltage fields. The positive
column plays the most important role in heating the gases in devices such as
arc gas heaters and metallizing equipment [8]. However, the anode and cathode
sheath regions strongly control the stability of the electrodes and location
of the positive column, and thus each phenomenon must be well understood in
the design of arc gas heaters or plasma deposition spray guns.

     The electric arc is the energy source for all plasma arc heaters and
spraying equipment. In both applications, a source gas is passed through the
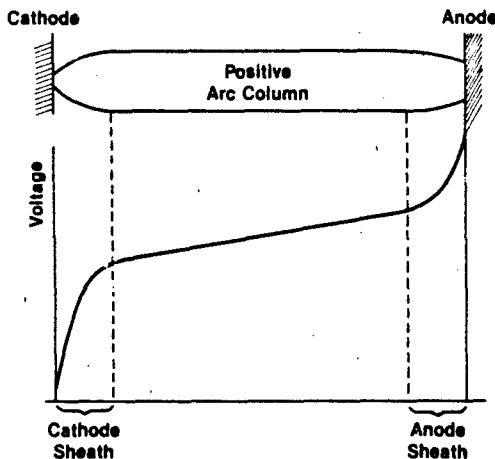
FIGURE 5-8 Schematic representation of electric arc.

arc for heating and producing an extremely hot "plasma" jet, and it is important to get the most efficient heat transfer to the gas that passes through the arc [9]. Improvements in arc/gas heat transfer have been achieved by constricting the arc in a small chamber through which the gases pass. The gas cools the periphery of the arc, reducing the conductivity and concentrating the current into the "core" of the arc; this arc constriction greatly increases the arc "core" temperature and is called "thermal pinch." Increased current density further concentrates or stabilizes the arc. Different types of arc stabilizations are used in the arc gas heaters: wall, gas sheath, vortex, water, and magnetic stabilization have all been utilized for this purpose. Except for magnetic stabilization, all of these types of stabilization cool and constrict the periphery of the arc (positive column). Most commercial plasma spray deposition equipment utilizes vortex-stabilized arc designs. Extensive work has been done on modeling these types of constricted arcs [10-12] and temperature profiles have been both calculated and experimentally measured [13-16]. Depending on the arc gas composition, temperatures in the arc have been found to range from 10,000 to 50,000 K.

Particle/Plasma Interactions

To achieve high-quality deposits, it is imperative that a large fraction of the particles be molten upon striking the substrate. An understanding of the melting process in plasma-arc spraying requires knowledge of the following: theoretically or experimentally determined temperature profiles in the plasma stream; the dwell time of the particle in the plasma stream, which in turn will depend on plasma jet velocity, particle size, shape, density, and velocity and plasma gas temperature via its effect on gas properties (density, viscosity, etc.); and the mechanism of heat transfer from the gas stream to the particles. It has been pointed out in previous chapters that there is a need for diagnostics to measure and evaluate parameters such as those listed. Much work is needed in characterizing the plasma state as well as the interaction of particulates with the plasma flame.

Plasma Gas Temperature and Velocity

The temperature (heat content) and the velocity of the plasma stream
depend on the nozzle geometry and on the operating conditions of the plasma
spray gun, i.e., arc power, gas composition, gas flow rate, and spray-vessel
pressure. For a plasma jet of relatively low gas velocity (Mach $<<1$), the
temperature and the velocity at the nozzle exit can be theoretically
calculated. The mean plasma gas velocity at the nozzle exit can be derived
and is as follows [1]:

$$V_g = 2 \, \Delta p \, A_n / \dot{M}_g \, [1 + (Ma^2/r)] \tag{1}$$

The mean plasma velocity, temperature, and density at the nozzle exit can all
be calculated from the experimental process parameters, i.e., the arc power,
cooling water loss, gas mass flow rate, and the calculated $H = f(T)$
relationship for the gas composition in use.

Theoretical prediction of the plasma jet temperature and velocity
distribution as a function of distance along the jet axis is difficult, and
thus these parameters are measured experimentally. Although spectrometric
techniques have been used for measuring plasma temperatures, the most often
used technique employs enthalpy probes. Plasma gas velocities have also been
measured using transient total impact probes, water-cooled probes, and laser
Doppler anemometry (LDA). The first two techniques require an estimation of
the gas temperature (and hence density) at the point of measurement. Plasma
gas velocities using the LDA technique are measured by seeding the gas with
small particles, of approximately 1-3 μm; it is assumed that the velocities of
the particles at different locations represent the actual plasma gas
velocities. Typical temperature and velocity profiles for a N_2 plasma at 29
kW as a function of axial and radial distances are shown in Figure 5-9 [17].
These measurements are difficult, and the data obtained must be interpreted
with care because, as the plasma velocities increase, correction terms that
depend on the gas velocities have to be taken into account. Similarly,
difficulties exist with the LDA technique. Here small particles should be
used if they are to attain the plasma gas velocity. However, the smaller
particles are prone to easier melting and subsequent evaporation, so that it
is rather difficult to measure the velocity profiles in the hotter regions of
the plasma.

Although exact theoretical predictions of the effects of plasma operating
conditions on gas velocity and temperature are difficult, certain
generalizations can be made. Increasing the arc power for a constant gas
composition and flow rate will result in an increase in the mean temperature,
heat content and velocity of the plasma. For a fixed arc power, increasing
the gas flow rate causes a decrease in the mean temperature and heat content
of the plasma. However, for a given material and fixed power, there is an
optimum gas flow rate at which deposition efficiency is at a maximum. At low
gas flow rates, the arc diameter is large and hence the center plasma core has
a lower temperature and velocity. When arc-gas flow rates are higher than the
optimum, the plasma core temperature and enthalpy are higher, but the arc
radius is smaller due to the "thermal pinch effect." Consequently, a larger
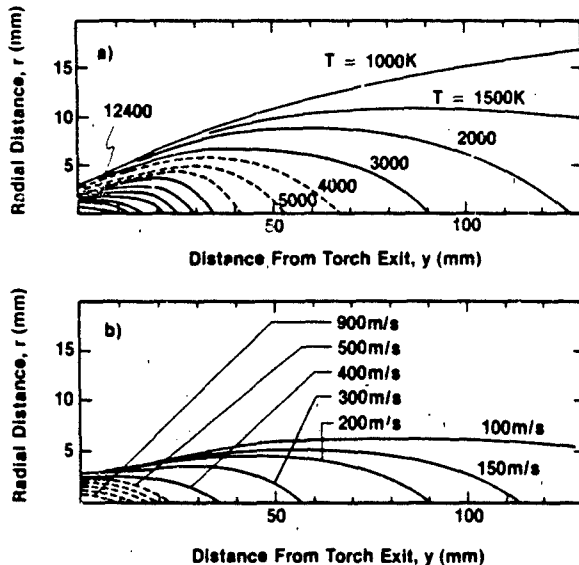
FIGURE 5-9 Temperature (a) and velocity (b) profiles for a dc N_2-H_2 plasma jet.

fraction of particles passes through a region where the temperatures are not high enough to cause particle melting and efficiency is again decreased. The temperatures in the plasma core also might be too high in this case and may cause evaporation of the particles.

Little information exists describing plasma deposition in reduced-pressure environments. However, significant analytical efforts have been applied to atmospheric plasma deposition, and this has provided a basis for further work on VPS. In applying the knowledge gained from atmospheric plasma deposition to VPS, it must be noted that the two processes are significantly different. There are additional complexities that need to be considered in VPS:

1. The lower chamber pressure results in gas velocities that are generally supersonic at the nozzle exit. As the gas velocities change from supersonic to subsonic at some distance from the nozzle exit, a shock wave develops. One therefore needs to know the effect of a shock wave on the particle velocity in the plasma flame. It is also necessary to consider the powder-injection technique that would be most effective in the entrainment of the particles in the plasma stream. Specifically, should the particles be injected before or after the shock wave, in the diverging, converging, or choked section of the nozzle?

2. As the spray chamber is at a low pressure, the plasma flame is more diffuse and longer than that in conventional plasma spraying. This results in a longer flight zone, which in turn affects the duration of particle heating or cooling, depending on the specific conditions.

Particle Velocity in the Plasma Jet

Powder particles upon injection into the plasma are accelerated by the jet due to drag forces and their velocity increases, whereas the velocity of the plasma jet decreases due to cooling and entrainment of the surrounding gases. At some distance from the plasma nozzle, the particle velocity will be greater than the gas stream velocity, and thus the particles will be decelerating. Neglecting radial and angular velocity components, the acceleration of a sphere in a viscous steady flow is given as

$$\frac{dV_p}{dt} = \frac{3}{4} \frac{C_D \rho_g}{D \rho_p} (v_g - v_p)|v_g - v_p|$$

(2)

The drag coefficient, C_D, a function of the particle's velocity relative to the surrounding gas, is the sum of two different drag terms: the frictional drag (viscous drag) and the pressure drag [18]. At low velocities the frictional drag is the predominant term and hence the drag coefficient is mainly dependent on the Reynolds number. At high velocities (> Mach 0.5), the pressure drag predominates, and the drag coefficient is mainly dependent on the velocity (relative to the surrounding gas) of the particles [18]. The Reynolds number is equal to $\rho_g \frac{|v_g - v_p|D}{\eta_g}$, where η_g is the dynamic viscosity of the plasma gas. Different values of the drag coefficient, C_D, have been used in the plasma literature, depending on the assumptions made regarding the particle velocity relative to the plasma gas.

The axial particle velocity profiles calculated using the above formulations show good agreement with experimentally determined velocities [19] (see Figure 5-10). However, in these theoretical calculations of particle velocities as a function of the radial and axial distances, one needs to know the changes in the gas stream velocity, the temperature, and the thermophysical properties (density, viscosity, specific heat, etc.) as a function of distance from the nozzle exit and radial distance from the plasma axis. This poses serious difficulties, since much of the data are not available.

Based on the experimental studies and theoretical analysis, it can be concluded that:

1. The peak mean velocity of the particles increases with decreasing particle size; however, at a large distance from the nozzle, the deceleration of the smaller particles is higher than that experienced by large particles [20,21]. As shown in Figure 5-11, the larger particles attain a steady state velocity value whereas the velocities of the smaller particles decay at an increased rate.

2. For the same particle size, the particles of a low-density material will achieve higher peak velocities, but their deceleration rate will be higher [21,22]. The mean kinetic energy for particles of the same size but different densities is also reported to be constant [22].

dp	Measured	Calculated
3 μm	▽	————
18 μm	△	—··—··—
23 μm	◇	— — —
39 μm	○	—·—·—·
48 μm	□	- - - - -
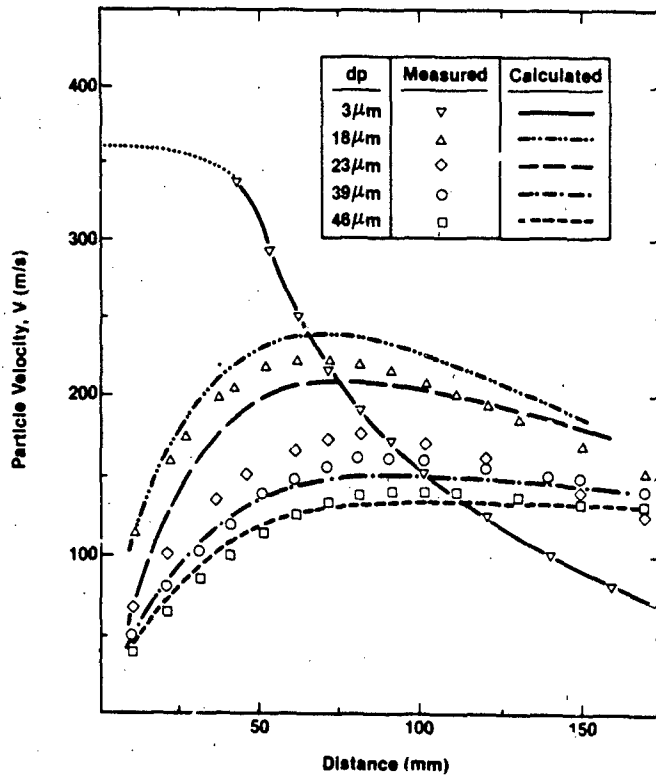
FIGURE 5-10   Measured and calculated particle velocities as a function of
               particle diameter and distance from torch orifice in an Ar-H_2
               plasma jet.

3.   Increasing the electrical power input to the plasma torch increases
the gas stream velocity and hence the mean particle velocity [20,21].

4.   Increasing the powder-injection velocity (up to an extent) causes the
particles to penetrate further into the high-velocity jet core and
results in higher mean particle velocities [20,23].

Gas-Particle Heat Transfer

The powder particles within the plasma are heated by a combination of
mechanisms: heat transfer by conduction through the boundary layer with or
without convection, radiation heating, electron bombardment, and atom
recombination at the surface [23]. When considering particle melting, heat
transfer across the boundary layer has generally been considered as the
dominant mechanism compared with the other heating mechanisms. The various
models of particle heating, available in the literature, vary in the number
and degree of simplifying assumptions made, but they can be divided into two
broad categories: models that assume that the thermal conductivity of the
material is high enough so that there are no temperature gradients in the
particles, and models that assume that temperature gradients exist in the
particles and are controlled by its thermal properties.
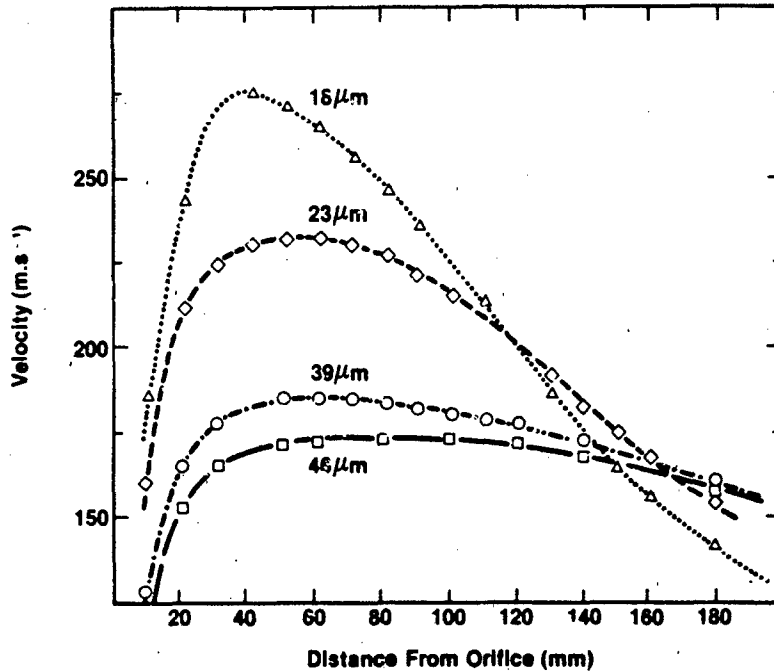
FIGURE 5-11   Mean particle velocity as a function of particle diameter and distance.

The governing equation for the heating of a spherical particle (through the solid or liquid phase) for the case when the particle temperature is uniform, is given by [24,25]:

$$\frac{dT_p}{dt} = \frac{6h(T_g - T_p)}{\rho_g DC_p}$$

(3)

During melting (for an isothermal transformation $dT_p/dt = 0$) the heat supplied by the plasma should be equal to the latent heat required to melt the particle [25].

The assumption that heat transferred to the particle surface propagates instantaneously through the particle cannot always be made, particularly when spraying particles of marginal thermal conductivity. Models that take temperature gradients in particles into account have been developed by Fiszdon and Lesinski [26], bourdin et al. [27], and Yoshida and Akashi [28]. The temperature distribution within the particle is governed by Fourier's equation. The applicable boundary conditions vary, depending on whether the particle is still in an unmelted state or if the particle surface temperature is above its melting point.

Heat Transfer Coefficient

The heat transfer coefficient, h, is calculated from the applicable Nusselt number, $Nu = hD/k_g$, where k_g is the thermal conductivity of the plasma gas. Different formulations of the Nusselt number that may be applicable under plasma spraying conditions have been reviewed by Kubanek et al. [29] and Waldie [30]. Various investigators have used Ranz and Marshall's [31] equation for calculating the Nusselt number for the plasma process:

$$Nu = \frac{hD}{k_g} = 2 + 0.6 \, Re^{1/2} \, Pr^{1/3} \tag{4}$$

and Pr (Prandtl's number) = $C_g \mu_g/k_g$, where C_g, μ_g, k_g are the specific heat, dynamic viscosity and thermal conductivity of the gas, respectively. In Equation 4 the first term is the contribution of the conductive heat transfer, whereas the second term represents the effect of the convective heat transfer. In application of Equation 4 the choice of a temperature at which the plasma gas properties are to be evaluated has to be made. Various authors have used different temperatures for calculating the mean plasma properties. The gas properties have been generally calculated for the mean boundary layer temperature $(T_g + T_s)/2$ to calculate the Nusselt number. A correction factor $\nu \underline{avg} \, 0.15$ has also been used to account for the steep temperature gradient. $\overline{\nu g}$

A recent approach to the problem has been to calculate the specific gas property in question as an integrated average over the temperature range considered [27].

Droplet-Substrate Interactions (Solidification)

Powder particles at the time they impinge on the substrate may be completely molten (droplets), only partially molten, or not melted at all. The partially melted or unmelted particles lead to low densities and deposition efficiencies. The partially or complet ly melted particles upon striking the substrate or the previously deposited layer undergo severe deformation as well as rapid solidification. Achieving high-density deposits requires that a large fraction of particles be in a molten state (droplets) when they impinge on the substrate.

There are three dominant phenomena that dictate the nature of the particle/substrate interactions: droplet spreading and morphology changes, heat transfer modes, a d droplet/substrate interface adhesion.

Droplet Morphology Change Upon Substrate Impact

In general, there are several ways in which the impinging droplet will behave; the morphological changes taking place depend on the extent of droplet melting and the nature of impingement. These various modes of behavior are described as follows:

- When the spray-deposited particle is not completely molten, the partially melted thin outer layer spreads on the deposit, whereas the unmelted particle core deforms into a pseudohemispherical shape. The unmelted core of the particle may also bounce-off, leaving a hollow center in the deposited layer.

- A completely molten droplet striking on the substrate spreads out radially in the form of a thin disk. In practice, however, the deposit is not uniform in thickness and the periphery of the particle is not circular. For modeling purposes it is usually assumed that the droplet spreads out radially and assumes the shape of a flat disk.

- When the resultant thin disk fails to establish a sufficiently strong bond with the contact surface, the outer portion of the disk either breaks off or the edges curl up and fold in toward the center. The curling-up of what initially started as a flattened disk is a consequence of the internal compressive stresses set up in the disk during freezing as well as a weaker adherence to the substrate at the periphery, as compared to the center of the disk.

In all of the foregoing situations, the impinging droplet experiences two simultaneous phenomena: solidification and radial flow into the form of a disk. The terminal thickness of the droplet is determined by the solidification rate of the droplet and by the conversion of droplet kinetic energy into surface and viscous energies.

A simple analysis of splat cooling (spreading and solidification of a droplet projected at high velocities onto a substrate) by Jones [32-34] indicates that the rate of the flattening of the droplet is orders of magnitude higher than the solidification rate. Spreading of the droplet is essentially complete before any significant amount of solidification has taken place, indicating that the spreading phenomenon can be treated separately. Thus the terminal thickness, S, of the disk (splat) is governed by the conversion of kinetic energy into surface and viscous work. Madejski [35] offers a more comprehensive treatment by taking into account the effect of solidification kinetics on droplet spreading, which includes viscous flow and surface considerations. Madejski introduces the parameter ε_m which is the ratio of splat diameter to the droplet diameter:

$$\varepsilon_m = \frac{2}{D} \frac{A}{\pi} = \frac{d}{D} \tag{5}$$

In essence, the splat thickness for a particular material being plasma-sprayed will mainly depend on the droplet velocity and on the degree of superheat via its effect on the surface tension and viscosity of the melt.

Heat Transfer

The quenching rate experienced by an impacted droplet is quite high, of the order of 10^5 to 10^6 K/s. The high cooling rate during plasma deposition influences the deposit properties; for example, microstructural

variables and parameters such as degree of supercooling possible, deposit grain size and dendrite arm spacing, and the presence of metastable phases, supersaturated solutions, or glassy phases. The cooling rate experienced will also influence the interparticle and particle/substrate metallurgical bonding (solid state diffusion or substrate fusion). Moreover, from a practical point of view the maximum deposition rate will be dictated by the realized cooling rate at the substrate interface. This is particularly important in the case where thick deposits must be produced.

When interface-controlled heat transfer is dominant, there is poor thermal contact between the splat and the substrate; the Biot No. <<1 and the temperature gradients in the splat and substrate can be neglected. Assuming that solidification occurs immediately below the melting point (supercooling is absent), then the following equation applies above and below the isothermal delay time at the melting point [36]:

$$\frac{dT_d}{dt} = \frac{h(T_{sub} - T_d)}{S\rho_p C_p} \tag{6}$$

When the Biot number is large ($h \to \infty$) there is no discontinuity in the temperature at the splat/substrate interface (or previously deposited layer) and relatively large thermal gradients exist in the splat and the substrate.

It is difficult to ascertain for a given particle-droplet/substrate system whether heat transfer is interface contact, ideal, or intermediate between these two ranges, since the degree of interface contact (i.e., particle-substrate or particle-particle adherence) depends on numerous process variables, such as particle velocity, degree of superheat, substrate surface finish, and temperature, in addition to the chemicophysical properties of the splat and substrate materials. Furthermore, the presence of surface oxides or splat edges curling upward will reduce the heat-transfer coefficient and therefore reduce the expected cooling rate. Plasma spraying onto a polished surface generally causes a weak deposit/substrate bond due to peeling of the splat edges. TEM studies on splat cooling have indicated that the direction and mode of heat transfer are much more complicated. The results of one study indicate that heat is extracted through the substrate in the core region (which is in contact with the substrate) whereas the rim section solidifies by conducting heat to the core region [37]. The mechanism of heat transfer as proposed by Safai and Herman [37] for a splat whose rim is not in contact with the substrate is shown in Figure 5-12. A systematic study of the particle/substrate or interparticle interface heat transfer coefficient, h, as a function of the plasma spraying process variables has not yet been carried out.

Particle/Substrate and Interparticle Adhesion

The deposit/substrate and the interparticle adhesion are of great concern since (a) the degree of contact between the particles or between the droplet and the substrate affects the interface heat transfer coefficient, h, and thus the cooling rate experienced by the deposited splat and (b) the nature of

Spraying
Direction

Spherical Particle
(Before Impact)

Liquid Flow

Core

Thin Electron Transparent
Region

Rim

Heat Flow

Heat Flow

Heat Flow
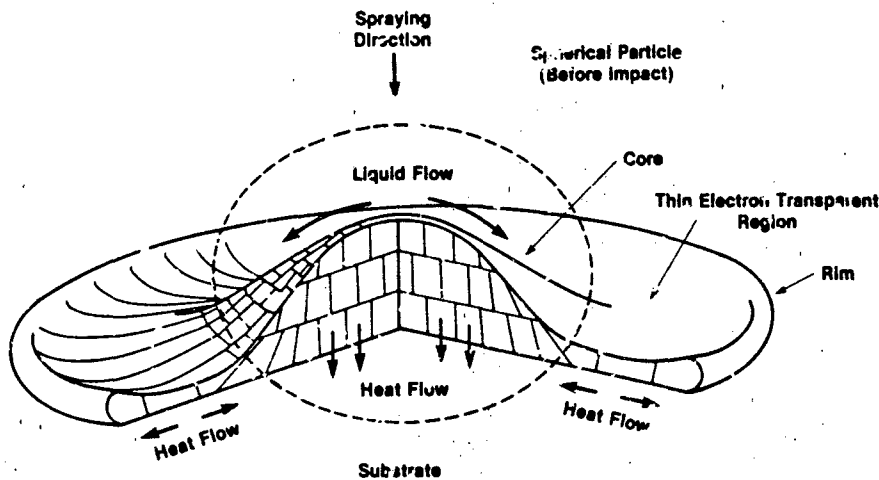
Substrate

FIGURE 5-12   Schematic diagram of a particle after impinging onto a flat
surface.

adhesion governs the effectiveness of the sprayed deposit as a protective
coating. A weak deposit/substrate bond will cause spalling of the deposit
under thermal/mechanical loading as well as corrosion failure.

The interparticle (and deposit/substrate) adhesion mechanism can be
classified into three major categories (it must be noted that more than one
mechanism might be operational):

- Mechanical bonding: A molten particle striking an already solidified
  splat or a roughened surface, given that it has sufficient fluidity,
  will assume the surface topography. The mechanical interlocking
  between the protrusions of the deposit and substrate will lead to
  mechanical adherence.

- Metallurgical bonding: Metallurgical adherence is the result of
  formation of an interdiffusion zone or an intermediate compound
  between the sprayed material and the substrate.

- Physical bonding: The action of the Van der Waal forces between the
  deposit and substrate material is termed physical bonding.

The bonding between the coating and substrate is generally a result of two
or more bonding mechanisms operating simultaneously; however, the degree to
which a particular mechanism is operating is a strong function of the
materials involved and the process variables (droplet and substrate
temperatures, droplet velocity, surface finish of the substrate, etc.).
Surface topography of the substrate is considered a major variable affecting
the degree of mechanical bonding between the deposit and the substrate. Grit
blasting, surface grooving, and undercutting of the substrate have been

used to promote interlocking between the coating and the substrate. It is hypothesized that, besides increasing the mechanical interlocking, surface working of the substrate exposes more clean fresh metal for bonding [38] and also increases the defect structure of the substrate surface, thereby increasing its reactivity with the impinging droplet.

CURRENT RESEARCH AND DEVELOPMENT

Plasma deposition is a very complex phenomenon requiring the control of many variables in order to produce high quality deposits. Many of these variables are not well understood and require additional attention. Among these is a better understanding of melting and solidification during plasma spraying. For the sake of analysis, melting and solidification have been discussed separately. In reality, however, the two phenomena are highly interrelated, and the extent of plasma-particle interaction has a dominant effect on particle-substrate interaction. For example, the momentum, viscosity, temperature, thermal conductivity, and size of the impinging particles (droplets) greatly affect the solidification process at the interface with the substrate.

It must be remembered that the entire plasma deposition process occurs in a highly dynamic environment. The particles being sprayed are not of the same size and hence follow different trajectories through the plasma jet. In applying any of the governing heat-transfer equations, one must take into account the changes in the physical properties of the gas and the applicable drag and heat-transfer coefficients because of the spatial variation in the plasma gas velocity and temperature. A review of the literature shows that there is no general agreement with respect to the applicable drag and heat-transfer coefficients for plasma-spraying conditions. Further work is needed. Most investigators have used relationships developed (via dimensional analysis and empirical correlations) for relatively large particles in gas streams of low temperatures and velocities. It is only recently that Sayegh and Gauvin [39,40] have analyzed the problem of heat transfer to a sphere, taking into account the changes in gas properties in the vicinity of the sphere owing to the steep temperature gradient existing there. Moreover, the available experimental data are mainly for stationary particles of relatively large size (2 to 6 mm) and no attempts have yet been made to show that the correlations obtained are valid for the smaller particles used in plasma spraying (typically 40 μm). In a review paper, Waldie [30] has stipulated that for smaller particle sizes (and in the limit as the particle size approaches the mean free path of the plasma gas) noncontinuum effects become significant and the Nusselt number would be lower than that calculated by any theory based on continuum mechanics. That this is indeed the case has been shown for atmospheric plasma spraying by Chen et al. [41]. With plasma spraying under a reduced pressure environment (as in VPS) these noncontinuum effects will be even more dominant and will cause significant lowering of the momentum and heat transfer to the powder particles [42]. Experimentally measured particle velocities in the VPS process are reported to be much lower than expected from calculations based on continuum mechanics [43].

Droplet-substrate interactions in plasma deposition parallel those already established for various types of splat cooling. Aspects not hitherto considered include consideration of transient effects during and after

spraying and their effect on deposit structure and properties. Droplet shape immediately after impact has been shown to influence both cooling rate and metallurgical bonding quality. Additional studies are clearly required to better define the range of droplet shapes that can occur during plasma deposition and to determine whether preferred shapes can consistently be controlled. Substrate temperatures will also affect droplet shape and bonding, but their effects have not yet been systematically evaluated. The effect of the relative gun-to-substrate motion also needs to be studied for its influence on substrate temperature and the relative uniformity of the deposit that can be achieved. The allowable impact angles for droplets impinging upon the substrate need to be evaluated if parts having complex shapes are to be manufactured.

Off-design operation of the plasma gun will affect particle melting, solidification, and deposition problems. This occurs in a real sense during actual processing, owing to anode wear by arc erosion and, to a lesser extent, by fluctuations in power supplies and associated control equipment. The challenge for the success of plasma deposition as a fabrication method for high-performance components may well include the need for a low level of process sensitivity to off-design conditions. A better understanding of the importance of these effects and how they can be controlled is required before high-performance structural shapes can consistently be produced by plasma deposition.

The technical challenges are clear, as are the rewards for meeting them. Plasma deposition, especially in low-pressure environments, is one of the few processes by which fully dense, near-net-shape structures can be produced, with rapid solidification and consolidation combined in one step.

NEW OPPORTUNITIES

Plasma Spraying

Historically, research and development in plasma spraying have been concerned primarily with (a) gun designs (power levels, nozzle shapes, cooling schemes, electrode life, focusing of plasma flame, etc.), (b) particle injection techniques (upstream vs. downstream, injection angle, powder mixing, exothermic reactions), (c) environmental controls (inert gas injection, shrouding, reduced pressure), and (d) metallurgical consequences of varying critical process parameters (jet exit velocity, temperature profile, powder spray pattern, melting rate, droplet quench rate, etc.). There is little doubt that continuing research and development along these lines are needed to further optimize plasma spraying technology. In addition, it seems appropriate to augment such activities with new initiatives that are targeted on specific problem areas or are aimed at exploiting new types of powders as they become available.

ID Torch Design

There is an urgent need for a convenient method to apply protective coatings to the ID of pipes. Adaptation of current gun designs to ID units is probably not workable. New designs will have to be developed, e.g., it has been proposed that pipe internals be coated by exploiting the radially

symmetric spray pattern developed in the impingement zone of two oppositely directed plasma spray jets.

Technology Transfer

The most extensive use of plasma spraying has been made in the gas turbine engine industry. A need exists to transfer this technology, including new materials and processes, to other industries, where it would greatly benefit productivity through improved performance and reduced material cost. For example, industry at large would derive substantial benefits from applying advanced plasma sprayed coatings to conventional low-alloy substrate materials. In general, this will necessitate further development of robotics and associated hardware in order to apply overlay coatings to large, complex surfaces such as chemical processing vessels, storage tanks, and pipe reactors.

Efforts should also be made to adapt technology already established in Japan (automobile engine valves), Western Europe (piston coatings) and the Soviet Union (catalyst coatings in diesels) to our own commercial internal combustion engines. Along with this, new capabilities for underwater plasma spraying (firmly established in the Soviet Union) need to be developed. In this regard, a worthwhile target would be to perfect a plasma sprayed "antifouling" coating for ships' hulls to reduce drag.

Real-Time Control

To achieve reproducibility in plasma spraying, real-time process control will be necessary. Efforts should be made to perfect fast-response sensing devices to obtain the real-time enthalpies necessary for process control. New instrumentation techniques must be developed that are capable of handling the high temperatures of the plasma stream and that can measure temperatures, gas velocities and particle velocities.

Post Deposition Treatments

For many critical application, plasma sprayed deposits are inadequate. This is because the deposits are lacking in density or may not be sufficiently well bonded to the underlying substrate. To overcome these deficiencies, post-deposition treatments such as laser melting (glazing), hot isostatic pressing, rapid omnidirectional compaction, or shot-peening need to be investigated. Some work has already been done on combining plasma spraying and shot-peening in a new "spray-peening" process.

Rapidly Solidified Powders and Ribbons

The availability of rapidly solidified powders and ribbons in the amorphous or microcrystalline conditions presents further opportunities for generating unique microstructures in plasma sprayed deposits. Materials in either of these two forms can be fed continuously into the plasma flame and sprayed onto the substrate. However, to ensure that the initial metastable state is recovered during deposition, a high quench rate is necessary. Process modifications need to be devised to guarantee high quench rates, such as cross-blasting to direct the plasma flame away from the region of deposition on the substrate. By this means, it should be possible to generate amorphous coatings and even amorphous free-standing bodies.

Injection of CVD Precursors

The fabrication of fine particulates by injecting CVD precursors into a plasma flame is a familiar process. A good example is the synthesis of silica particles by thermal decomposition of organosilicon precursors in a plasma flame under oxidizing conditions. By reducing the residence time in the plasma, or by selecting precursors that have more sluggish decomposition kinetics, the plasma will contain molecular fragments (free radicals), as well as small particles, that will tend to react and form a continuous film on the substrate.

A particular advantage of this plasma/CVD process is its inherent flexibility. It is not hard to imagine the synthesis of dispersion-strengthened materials from mixed precursors, which have radically different decomposition kinetics. Again, possibilities exist for insitu fabrication of layered structures, simply by switching from one gas feed to another, as required. At high enough temperatures, with correspondingly short residence times, very high deposition rates should be attainable. Thus, it seems entirely practical to employ the plasma/CVD process in coating applications.

Near Net Shape Fabrication

The advent of vacuum plasma spraying has changed the picture fundamentally with respect to near-net shape fabrication. The supersonic velocities of the plasma flame, high deposition rates, and broad spray patterns characteristic of VPS permit the incremental buildup of sound (i.e., pore-free), bulk structures, as well as providing the microstructural and property benefits of rapid solidification processing.

Progress has already been made in the fabrication of prototype gas turbine engine components, e.g., combustors and airfoils. However, a need exists to apply this technology to the near-net-shape fabrication of general engineering components, such as bearings, extrusion dies, valve bodies, pipes, casings, and sleeves.

Plasma Transferred Arc Deposition

The evolution of plasma transferred arc deposition, as in the case of plasma spraying, has been paced by advances in torch design, powder feed capabilities, and environmental control systems. Today, efforts to improve on these capabilities continue, with the emphasis on computer control and powder delivery systems. Already, numerically controlled work stations for hardfacing simple geometrical shapes are available, and experimental robotic systems are being developed. Powder feed capabilities continue to improve, so that today up to four different powder feeds can be incorporated in systems of advanced design.

Considering the present status of transferred arc technology, it seems that further research and development should be directed toward achieving more reproducible microstructures via real-time process control and creating novel composite structures by exploiting mixed powder feeds.

Computer Control and Automation

Despite the real progress that has been made in computer control and automation, much still remains to be done. In particular, there is a need for a versatile, reprogrammable robotic system to apply hardfacing treatments to the variable geometries encountered in production operations, such as valve seats, and slide valve and bearing surfaces.

Novel Composite Structures

It has been demonstrated that, by effective control of the residence time in the molten pool during hardfacing, particles of TiC can be injected into the melt without undergoing complete dissolution. Thus, a unique composite structure can be produced that contains a high-volume fraction of TiC particles in a conventional alloy matrix. This is an exciting development in hardfacing technology, and efforts should be made to determine its applicability to other alloy systems of interest for wear applications.

Dispersion-Strengthened Alloys

At the present time, the only practical method for fabricating inert particle dispersion-strengthened alloys is by mechanical alloying. Typically such materials contain uniform dispersions of very fine oxide particles, or particles of other inert phases in a metallic matrix. The mixed powder feed capability of advanced transferred arc systems suggests a new approach that exploits the principles of displacement reaction processing. Thus two different feeds are rapidly mixed and melted together and in so doing react insitu to form the dispersion-strengthening phase. If the residence time in the molten state is sufficiently brief, the new phase will remain as a fine dispersion, and the resulting solidification product will be dispersion-strengthened. Many interesting alloy systems need to be examined, including Y_2O_3 dispersion-strengthened superalloys and Al_2O_3 dispersion-strengthened copper.

Post-Deposition Treatments

As in the case of plasma spraying, possibilities exist for further improving properties of the deposited material by post-deposition surface treatments. An interesting case is the application of laser surface remelting to the relatively thick transferred arc hardfacing deposits in order to achieve rapid solidification of the alloy matrix without significant dissolution of the dispersed phase. Selective melting of the matrix in this way, with or without the benefit of subsequent heat treatment, opens the door to possibilities for optimization of the matrix properties without sacrificing the benefits derived from the hard-phase dispersion.

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CHAPTER 6

THERMAL PLASMA SYNTHESIS AND CONSOLIDATION

The use of thermal plasmas for the preparation and processing of metal and ceramic powders and their mixtures has proved to be commercially attractive in a limited number of instances and is a subject of continuing interest. Current applications include the production of submicron powders, particularly refractory ceramics, the spheroidization and densification of powders and presintered conglomerates, the preparation of high-purity materials and metastable phases, the deposition of abrasion and corrosion-resistant coatings, and the production of sintered materials. To find commercial application, the relatively higher processing costs of using plasma processing must be offset by some superior materials' properties. Review articles on these subjects include those by Mahe [1], Samsonov [2], Drost [3], Waldie [4], Sayce [5], and Thorpe [6].

In this chapter the following topics relevant to thermal plasma synthesis and consolidation are considered in turn:

1. The equipment available and necessary for synthesis and consolidation.
2. The general features of processing powders in thermal plasmas.
3. The interaction of injected gases and particulates with the plasma.
4. The production of submicron particles of refractory materials.
5. Material dissociation, spheroidization and densification by plasma heating.

Within each of these topics, the status of our current understanding and of current research and development efforts are discussed.

EQUIPMENT REQUIRED FOR SYNTHESIS AND CONSOLIDATION

The equipment necessary for plasma processing is relatively inexpensive, and the required plasma generators are, in many cases, commercially available. Alternating and direct current heaters and rf plasma generators have been developed in a wide variety of designs and over a power range from a few hundred watts to 50-MW [7].

As an example, Figure 6-1 shows the electrode assembly of a convection-stabilized arc plasma reactor [8]. For controlling the arc atmosphere, the electrode assembly is mounted in a reaction vessel. In this configuration, the arc is operated between a sharp-tipped cathode and a graphite ring-shaped anode. The cathode assembly contains three convergent flows arranged concentrically around the cathode. The flow passage adjacent to the cathode supplies the gas that is necessary for feeding the cathode jet, followed by several orifices for the injection of particles. The outermost passage carries the shrouding gas for convective stabilization of the arc. This design is similar to the "fluid convection cathode" introduced by Sheer et al. [9,10].
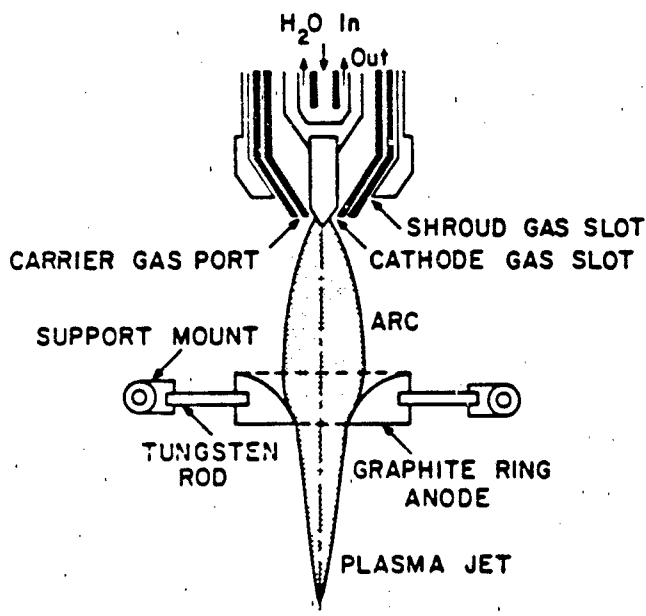
FIGURE 6-1   Electrode assembly of a convection-stablilized plasma reactor.

Figure 6-2 shows calculated and measured isotherms [8] of this arc operated in argon atmosphere. Temperatures close to the cathode tip may exceed 20,000 K. This design lends itself to extremely high reaction rates because of the high temperatures to which the injected particles are exposed.

Another experimental plasma reactor is shown in Figure 6-3 [11]. The basic parts of the reactor are a conventional swirl-stabilized plasma torch, a reaction duct, and a collection chamber. Reactants are injected into the plasma stream through an injection ring immediately downstream of the torch nozzle. Chemical reactions take place in the segmented 10-mm-diameter graphite reaction tube; its length can be adjusted by adding or removing a number of graphite segments. The plasma torch is operated with argon in either the nontransferred or the transferred mode. In the nontransferred mode, particles are injected into the tail flame (plasma jet) emanating from
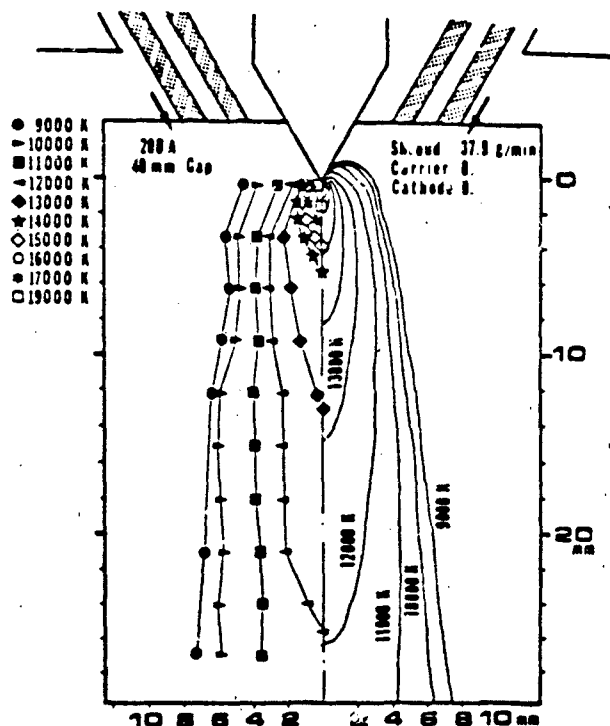
FIGURE 6-2   Measured and calculated isotherms in a convection-stabilized arc
              plasma reactor (argon, p = 1 atm).

the plasma torch nozzle. The purpose of the transferred arc is to increase
the temperature in the first section of the reaction duct in order to obtain
higher reaction rates. Downstream of the auxiliary anode the peak temperature
of the plasma decays very quickly, from approximately 12,000 K to 3,000 K over
a distance of approximately 2 cm, providing a rapid quenching of the reaction
products. Further quenching can be obtained by radial injection of argon gas
through the quenching ring located at the end of the reaction duct. Past this
ring the quenched products enter the expanded volume of the cold-wall
collection chamber.

    Figure 6-4 refers to a typical rf plasma torch [12]. Since the
appearance of the plasma resembles that of an arc, this discharge is also
known as an "induction arc" or as an "electrodeless arc." The plasma is
separated from the induction coil by a quartz tube, which may be replaced by a
ceramic tube, or by a longitudinally slotted metal tube [13]. Since the
plasma is not in contact with electrodes, this type of plasma torch is of
particular interest if extremely pure products are desired. In addition, the
rf torch provides more flexibility in terms of the size of the produced plasma
volumes compared with arc torches.
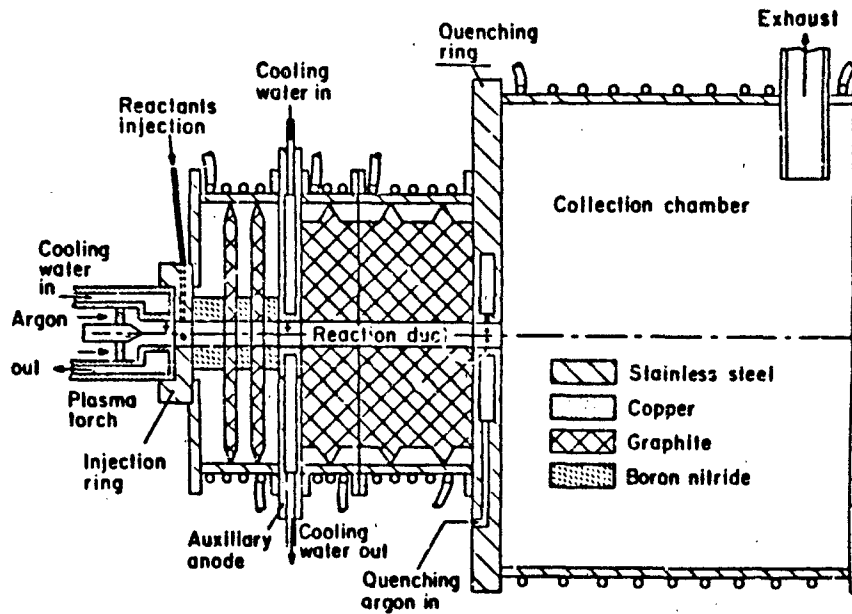
FIGURE 6-3   Plasma reactor for transferred and nontransferred arc operation.
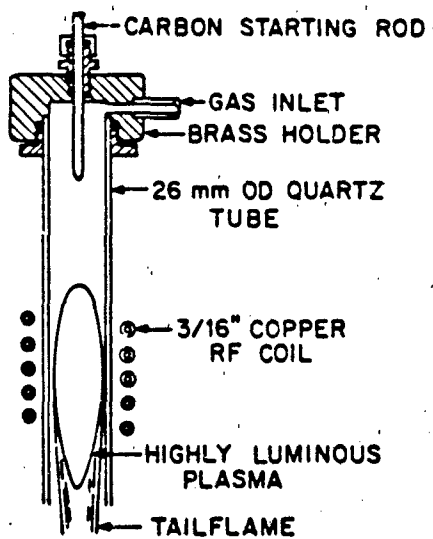
FIGURE 6-4   Induction-coupled rf plasma torch.

In contrast to arcs that exhibit a temperature maximum in the center, inductively coupled rf discharges show off-axis peaks, as indicated in Figure 6-5 [14]. In general, the maximum temperatures in rf discharges are substantially lower than those in arcs. The average temperatures range from around 4,000 K to approximately 10,000 K.
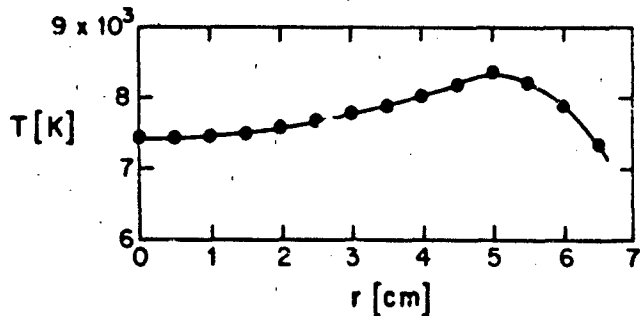
FIGURE 6-5   Typical temperature distribution in an induction-coupled rf plasma.

The ac and dc arc heaters usually are operated with high mass flow rates and high gas velocities (100 to over 1000 m/sec). The residence times of the gases in the hot reaction zone are short (of the order of a few milliseconds, or shorter), and strong axial gradients result in extreme heating and cooling rates (10^6 K/sec). High-frequency plasma generators usually have a more uniform temperature profile (Figure 6-5), smaller temperature gradients, and lower flow rates (<200 m/s) and therefore lower heating and cooling rates and longer gas residence times [15]. To obtain some of the advantages of both designs, a few hybrid plasma generators have been developed [16]. Most of the plasma generators presently available are not optimized for a single process. Recent progress in the description of process kinetics [17] will help in defining the optimum conditions for a certain reaction and consequently, in the optimization of the plasma generator for a specific application. Scaling laws will have to be established for the design of plasma generators in a size required by process optimization and economics. In this context electrode erosion in general and compatibility of specific electrode materials with certain reactant/product mixtures in particular is of great importance. Electrode erosion may lead to contamination of an otherwise very pure substance, or it may increase downtime of a certain reactor. A better understanding of the erosion process would aid in the successful development of plasma reactors.

Another consideration in hardware development is the possibility of retrofitting the plasma reactor into an existing process plant.

FEATURES OF POWDER PROCESSING

Plasma processing of powders to produce altered or reacted powders is a sufficiently novel technique and many features are not well appreciated.

- The thermal plasma is very hot, on the order of 10^4 K. Injected chemical species, especially in the gaseous phase can also reach or come close to these temperatures.

- At these elevated temperatures, reaction rates are much faster than those encountered in conventional processing. Reactions that might require hours under conventional conditions are completed in fractions of a second.

- Because of the relatively high velocity of injected gases and of particulate matter into a thermal plasma, the entire process of heating, melting, evaporating, and reacting must be completed in a few milliseconds. Successful application of plasma processing will depend critically on the ability to control the reactant-particles' trajectories and temperature histories in the reactor. Failure to do so will result in inhomogeneous products [18].

- Quench rates for product powders are also very rapid. From measurements and/or calculations of the temperature and velocity profiles within the reactor, one can show that typical cooling rates for products of dc reactors are in the range from 10^4 to 10^6 K/sec.

- Because of the rapid nucleation rates, the product powders tend to be submicron-sized. This has a distinct advantage for some applications where submicron sized powders are desired, but it is a distinct disadvantage in the broader area of powder metallurgy, where larger particles are required because of ease of handling and more resistance to contamination.

- Because of the rapid nucleation rates, the product powders may not be in equilibrium. For example, the product may be amorphous or may be the high-temperature phase. Heterogeneous nucleation, caused by simultaneous condensation of two phases, can cause additional metastable structures.

- The submicron powder size is ideal for detailed engineering and scientific studies of initial particle nucleation and growth from gas-phase reactions.

- Processing is continuous and relatively easy to control and monitor, and thus it lends itself to automation (robotics).

INJECTION OF GASES AND PARTICULATES INTO PLASMAS

A key problem in thermal plasma synthesis and consolidation is the incomplete understanding of the interaction of gases and particulate matter with the plasma. Particulate matter is usually injected into a plasma by means of a carrier gas. This carrier gas may be inert or it may participate in the desired chemical reaction.

The process of gas injection and gas mixing has been extensively studied for gases at lower temperature levels at which the transport properties may be

taken as constant [19-23]. Earlier work, particularly by NACA in the late 1940's and early 1950's is summarized in the references cited. Only recently, basic studies of the injection and mixing process involving hot plasmas and cold gases have been initiated [24]. The injection and mixing process is, in this case, more involved because of the drastic changes of the transport properties with temperature.

In the development of arc gas heaters, lower average temperatures have been achieved by rotating the arc in a continuous flow of cold gases. As an example, Figure 6-6 shows such a reactor in which the arc rotates from the action of a superimposed magnetic field [25]. This approach may give rise to serious electrode problems if chemically reacting gases are utilized. Injection of such gases into the plasma emanating from a plasma torch eliminates these problems.
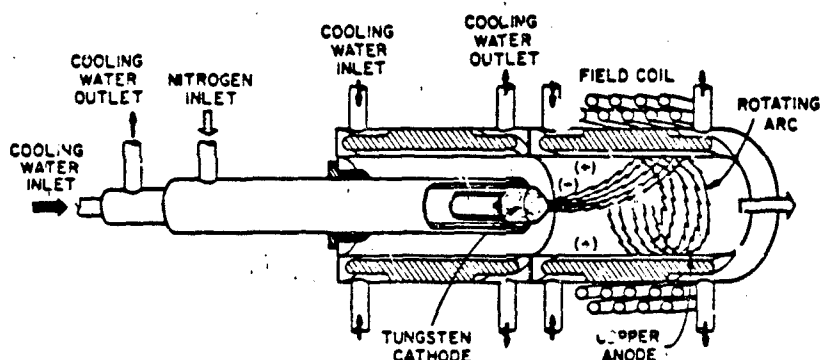
FIGURE 6-6   Schematic of a magnetically spun arc in a wide-nozzle plasma torch.

In comparison to the injection of inert gases as carrier gases and/or diluents into thermal plasmas, the injection of chemically reacting gases for forming or breaking up certain chemical compounds may be even more important. It is obvious that the simultaneous chemical reactions add further complexity to this complicated mixing process.

All heterogeneous plasma synthesis as well as plasma spraying applications involve the feeding of particles to a reactor or the collection of particles from it or both. Plasma treatment is an expensive unit operation in which high conversions per pass are a prerequisite for economic viability. The extremely short residence time associated with most plasma applications (10^{-3}sec) makes it imperative that high degrees of both spatial and temporal uniformity are achieved in particle feeding if high conversions without overreaction are to be obtained. Since the majority of plasma treatments are heat transfer controlled, a minimum of cold gas should be used to inject the particles.

No commercial feeders are completely suitable for plasma processes. Both laboratory- and full-scale plasma torches require feed rates that are much smaller than those used in more conventional processing methods. Scaling up from laboratory results to full-scale equipment can lead to large discrepancies if a totally different type of feeder is used for the two. Finally, some processes require operation in carefully controlled atmospheres, which is often difficult with conventional equipment.

Injection of particulate matter into thermal plasmas is a commercially practiced technique in connection with plasma spraying over a wide spectrum of materials ranging from plastics to refractories. (See, for example, Figure 5-3 in Chapter 5.) Details of the particle injection and of the processing occurring within the plasma, however, are still not well understood despite increasing efforts in this field [26-37].

Finally, the question of product collection and product separation should be addressed. Many plasma processes produce a valuable solid entrained in a very-high-temperature gas stream. Since the loss of any of this product will add to the operating cost, it is evident that gas-solid separation at high temperature is very important for the success of a plasma process.

The only systems available for gas-solid separation at high efficiency for very fine particles are filters and electrostatic precipitators. Both of these have rather modest upper operating temperature limits, which means that a quench of the plasma stream is required before the separation can be carried out. Many plasma products are pyrophoric because of their small size and reactivity. Here again, special controlled-atmosphere systems may be required.

Among the various plasma processing routes utilizing particulate matter, two major categories may be singled out:

1. Physical processing, wherein the plasma's heat induces phase changes, i.e. melting, evaporation, and also crystal structure changes.

2. Chemical processing, wherein the plasma induces one or more chemical reactions.

In the first category the heat transfer process is of particular importance; it is much more complex than in an ordinary gas because of the presence of charged particles [37]. The boundary layer between a plasma and a solid or liquid body, for example, is no longer in a state of thermal equilibrium. Diffusion induced by extremely steep gradients of particle densities and temperature causes substantial deviations from chemical equilibrium, so that the boundary layer is in a more-or-less "frozen" state. In highly ionized plasmas such a "frozen" boundary layer gives rise to substantially higher heat transfer rates than one would expect in an equilibrium situation [37-38]. This fact is of great importance in actual applications in which high heat transfer rates are desirable. The high heat transfer rates allow a short dwell time of the particles in the plasma, which in turn means high throughput rates using relatively small plasma volumes. The high heat transfer rates during the dwell time of particulate matter in a

plasma as well as the high quenching rates imposed on the particulates as they leave the plasma may result in unusual material properties which cannot be realized by any other known process.

Processes falling in the second category are much more complex because, in addition to the physical changes typical for the first category, one or several chemical reactions may be induced, either on or within the particle itself or in the gaseous phase after evaporation. The kinetics of the various reactions is poorly understood, although attempts are under way to establish suitable models [39].

SYNTHESIS OF SUBMICRON PARTICLES

Increasingly, thermal plasmas are being used to process submicron powders of high-quality refractory materials. The plasma-processed powders are extremely fine (~ 0.01-$0.1 \mu m$). While not used frequently by themselves, the powders can be blended with coarse powders to improve densification in subsequent processing operations [40]. In some cases the submicron powders are directly sintered without blending. Silicon carbide (β-SiC) is one such example. Plasma-produced silicon carbide has superior mechanical and thermal properties in applications such as heating elements [41]. Nearly all binary refractory carbides and some refractory nitrides and oxides have been synthesized in plasmas by gas phase reactions [42-53]. Recent results also show that ternary carbides can be synthesized either from the elements or by direct reduction of the oxides and simultaneous carbide synthesis within the plasma reactor [54].

A number of submicron oxide powders have been produced in a plasma. Such powders have a wide range of uses in surface casting, high-density ceramics, pigments, catalysis and dispersion strengthening of metals [5]. Three plasma techniques have been explored: reaction of volatile metal chlorides with oxygen; evaporation and subsequent condensation of oxide powders; and evaporation of bulk oxides. Industrially, TiO_2 and high-purity SiO_2 are produced by the chloride process. Mixed oxides of chromia and titania or chromia and alumina have been processed by introducing mixed chlorides into the reactor [55,56]. Korman, et al. [10] found that plasma-processed silica has properties similar to silica commercially produced by other techniques. Fine silica is used in paint, polymers, and cosmetics.

A hydrogen plasma, created by a dc arc, has been used to heat vaporized metallic halides, which react to form submicron (0.1 to 0.5 μm) ceramic powders [57]. Small-scale production of SiC, TiC, and TiB_2 has been accomplished with a 125-kW pilot reactor. In the case to TiB_2, titanium tetrachloride and boron trichloride are mixed with excess hydrogen to yield the boride and hydrogen chloride. The resulting powder can be cold pressed and sintered. The TiB_2 thus produced has an electrical resistance in the range of 7 to 15 micro-ohms cm and has been shown to be useful for cathodes in the Hall process for alumina reduction.

Previous research shows that a wide variety of compounds and alloys can be directly synthesized in submicron powder form by plasma processing [58]. Injection of coarse powders into a plasma generally reduces powder size to

submicron sizes, although this seems not to be true for transition metal nitrides. Plasma synthesis also appears capable of combining a number of processing steps, such as oxide reduction and alloying, into one processing step, but this area has not been well researched.

PLASMA DISSOCIATION, SPHEROIDIZATION AND DENSIFICATION OF MATERIALS

The goal of preparing a known material in an easier way has been successfully accomplished in the synthesis of zirconia [59]. Plasma-dissociated zircon is prepared by passing zircon sand through a plasma furnace, which melts and resolidifies the sand as a spherical particle consisting of zirconia dispersed in silica. The zirconia is obtained by leaching away the silica.

Commercially, fine particles are being spheroidized in a plasma for a variety of applications, including materials with a controlled porosity, catalysts [60,61], abrasives, and materials to transfer ink in photocopiers. A wide range of different materials have been spheroidized, including oxides [61-66] and carbides [63,67].

In the case of refractory particles injected into a plasma stream, the spherical liquid droplets that are produced rapidly solidify upon cooling. This may be simply useful in producing free-flowing powders, but it may be more valuable in certain ceramics, wherein metastable forms, especially the amorphous state, are produced. Mullite and certain other aluminosilicates have been found to form as glasses in particle sizes $< 20 \, \mu m$. Such observations suggest the possibility of producing fully dense, ultra-fine grained ceramics by hot pressing certain normally crystalline ceramic powders in the glassy (viscous flow) condition, followed by controlled devitrification. Although this has not been accomplished to date, such research should be encouraged [68].

Plasma densification of presintered agglomerates of metals—e.g., W, Mo—and of carbide-metal mixtures—e.g., WC-Co—have been used to produce spherical, densified powders. If mixtures are used, prealloying or homogeneous composite particles are accomplished. The powders because of their spherical and smooth surface form, possess excellent flowability, which is beneficial to subsequent plasma coating operations [69].

It has been demonstrated that plasma sintering leads to higher densities in shorter times at lower temperatures than conventional sintering [70-74]. Plasmas generated in a microwave cavity and a hollow cathode have been observed to enhance the sintering rates of a number of oxide powders, e.g., Al_2O_3, BeO, and HfO_2. In the case of lithia-stabilized alumina beta, an induction-coupled plasma at atmospheric pressure has been used to produce sintered densities ≈ 98 percent of theoretical in times in the order of 90s [74,75].

CONCLUSIONS

The synthesis and consolidation of materials by thermal plasmas has largely been accomplished by iterative empiricism. To improve our

understanding and advance the technology, research and development activities are required that are directed toward:

- synthesis and consolidation equipment, which consider the specifics of the heat transfer process, plasma reactions, and reactor optimization;

- injection of gases and particulates into the plasma, which consider gas/particle/plasma interactions and systems for introducing chemically reactive gases and particulates;

- studies of submicron particle formation and growth in the plasma environment; and

- the rapid densification that can be accomplished by plasma sintering.

The most important opportunities for this technology appear to involve the production of submicron oxides, the elemental synthesis of carbides and nitrides, oxide reduction and alloy synthesis in one step, thermal plasma dissociation of compounds, spheroidization and densification of porous particles, and plasma sintering of ceramic powders.

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CHAPTER 7

PROCESSING OF MATERIALS
USING LOW-PRESSURE, NONEQUILIBRIUM PLASMAS

Low-pressure, low-temperature gas discharges (cold plasmas) are being
used in a diverse and expanding number of applications that have in common the
objective of modifying the surfaces of materials. These applications involve
a variety of interactions, both physical and chemical, of plasmas with solids
and cover a broad spectrum of topics bordering on many disciplines. It is not
our intention to provide here an inclusive or exhaustive coverage of the
subject matter; instead we will focus on a few applications that illustrate
some of th· unique abilities of plasmas to modify surfaces and produce
end-products with substantial technological and economic significance.

Modifications of solid surfaces arising from interactions with cold
plasmas can be broadly classified as follows:

- Surface Cleaning and Alteration--Cold plasmas are used to remove
  trace contaminants as well as to produce rearrangement of atomic or
  molecular configurations, usually in preparation for further
  processing of the surface. Examples include the removal of
  contaminants from substrates prior to film deposition [1] and the
  treatment of polymers to increase wettability or produce molecular
  weight changes in near-surface regions [2].

- Chemical Alteration--The chemical composition of surface and
  near-surface regions can be altered by interactions with plasmas.
  Oxidizing (e.g., by plasma anodization), nitriding, carbiding, and
  siliciding of metal or semiconductor surfaces are examples [2].

- Etching--Atom-by-atom removal of surface material can result from
  physical and/or chemical interactions with plasmas. Plasma-assisted
  etching methods, such as ion beam etching, plasma etching, and
  reactive ion etching, are increasingly becoming indispensable
  techniques for the fabrication of microelectronic devices,
  particularly silicon integrated circuits [3].

- Film Deposition--Plasmas are widely used for the deposition of thin films onto surfaces [4]. Deposited films serve various functions ranging from surface protection against corrosion and wear to active and passive elements in electronic, magnetic, or optical devices. Plasma polymerization, plasma-enhanced chemical vapor deposition, sputter deposition, and ion plating are the more important techniques employed.

- Texturing--Surface topography can be altered by interaction with a plasma. Both etc ing and deposition are usually involved in texturing.

The plasmas of interest for surface modification are low pressure ("glow") discharges. Operating pressures range from $\sim 10^{-4}$ torr to 10^{+1} torr, depending on the application. These plasmas contain free electrons, positive and negative ions, neutral atoms, and, in the case of molecular gases, neutral molecules and molecular fragments (including free radicals) produced primarily by electron impact dissociation. Average electron energies range from ~ 1 to 10 eV, while the energies of ions and neutrals in the bulk of the plasma are substantially less (~ 0.1 eV). Thus the plasma is effectively "cold" even though the electron energies correspond to temperatures up to 10^5 K. This rather unique nonequilibrium state of affairs makes such discharges particularly suited to a number of applications where technical considerations impose temperature restrictions. For example, the deposition of inorganic films to function as passivating layers in silicon integrated circuits has been carried out almost exclusively by plasma deposition because alternative techniques that can produce films of the requisite quality require temperatures incompatible with circuit metallization [5].

Surface modification results from energy transfer between a plasma and a solid surface. Energy can be transferred by optical radiation (UV photons are particularly important in some of the applications of interest), electron and ion impact, and neutral particle fluxes (free radicals are particularly important in certain applications). The energy is dissipated by a variety of physical and chemical processes, as will become apparent in the following section.

PROCESSES AND APPLICATIONS

In this section we describe several processes for modifying solid surfaces with plasmas that illustrate the various physical and chemical phenomena involved as well as the extremes in the status of present knowledge of the processes from relatively well-understood to relatively poorly understood.

Sputter Deposition of Films

Figure 7-1 shows a simplified cross section of a sputtering system. The target consists of the material to be deposited or from which the film will be synthesized in the case of reactive sputter deposition. A gas is introduced to the vacuum chamber at a pressure ranging from a few millitorr to about 100 mTorr, and a discharge is ignited by applying a dc or rf voltage of sufficient

VOLTAGE SUPPLY (-VE)

GROUND SHIELD
WATER-COOLED
BACKING PLATE
TARGET

— GLOW DISCHARGE —

SUBSTRATE HOLDER — VACUUM CHAMBER

GAS
INLET

VACUUM
PUMPS
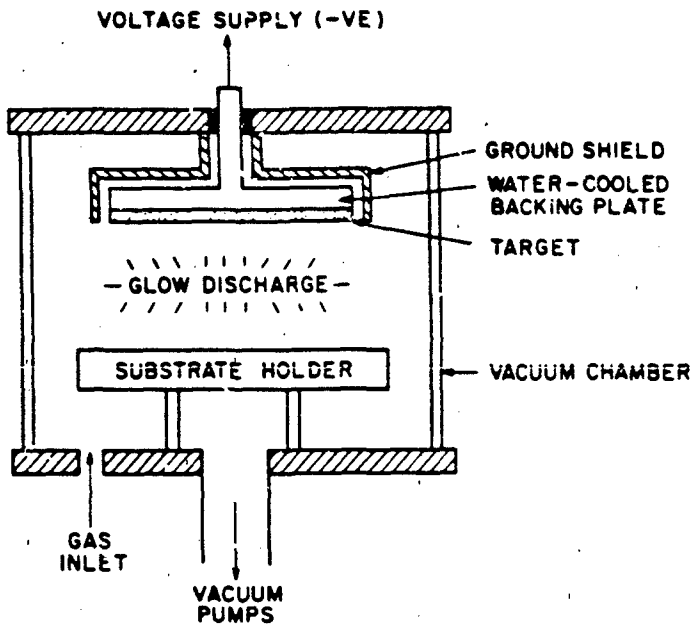
FIGURE 7-1   Cross section of a sputtering system.

magnitude.   The power is coupled to the target so that the target is
negatively biased with respect to the plasma. With proper system geometry and
grounding, most of the applied voltage drops across a narrow (≈ 1 cm) sheath
between the target and the plasma. Under these conditions, positive ions are
drawn from the plasma, are accelerated across the sheath, and strike the
target surface. When the arriving ions have energies exceeding a certain
threshold value (the sputtering threshold, typically tens of electron volts),
they can cause ejection of target atoms as they exchange energy and momentum
with the target. The ejected atoms condense on all surfaces they encounter.
Thus a film can be grown, atom by atom, on the substrate.

In practical systems, argon is most often used as the gas, and the
bombarding ions can have energies up to several keV. Reactive sputtering is a
useful variant where the gas used contains one or more constituents that can
react with the target material to form a compound. For example, TiO_2 films
can be deposited by sputtering Ti in O_2 or $Ar-O_2$ mixture; Si_3N_4 films
result when Si is sputtered in N_2 or NH_3 discharges.

In practice, use is often made of magnetic fields to enhance the rate of
sputter deposition in what is known as magnetron sputtering. The fields,
usually applied by fixed, permanent magnet pole pieces in close proximity to
the target, impart a helical motion to the free electrons of the plasma. This
has the net effect of increasing the electron path length, thereby causing an
increase in the number of ionizing collisions and the plasma (ion) density.
An added benefit of magnetron sputtering is that the number of high-energy

(secondary) electrons reaching the substrate after ejection from the target is diminished. This reduces substrate heating considerably and makes possible the deposition of films onto thermally sensitive substrates, such as plastics, without elaborate means of heat dissipation [6].

Sputter deposition is a relatively well-characterized, well-understood process. It offers certain advantages in comparison to other film-formation techniques. For example, sputtering is applicable to all materials, provided an appropriate target can be fabricated. Furthermore, compounds and multi-element materials can be sputtered and films deposited with the stoichiometry of the target. An additional advantage is that the sputtered atoms arrive at the substrate typically with much greater energy than is obtained with other deposition techniques. This often results in improved adhesion of films.

Sputtering is widely employed in the metals, plastics, optics, and microelectronics industries using a variety of commercial equipment. Applications include decorative and protective coatings, dielectric films for insulation and optical components, metallic films for magnetic or electronic circuit elements, and wear coatings for tools. The magnitude of the effort in this area is indicated by the fact that the sale of sputtering equipment to the semiconductor industry alone is estimated to reach \$300 million per year by 1985.

Sputter Etching

The sputtering phenomenon is also used to remove surface material under conditions quite similar to those described for sputter deposition. In essence, the target becomes the workpiece. A noble gas discharge is usually employed and material is removed by a strictly physical interaction between energetic ions extracted from the plasma and the solid surface. An important feature of this interaction for some applications is that ions arrive predominantly at normal incidence to the surface, and thus the etching is strongly directional (anisotropic). This is particularly pertinent to certain microelectronics applications where etching is used to transfer very fine (micron-sized) patterns into the surface by use of an expendable, patterned masking layer, typically an organic photoresist. A high degree of etch anisotropy ensures that the etched feature will not undercut the mask and diminish pattern fidelity [7].

On the other hand, sputter etching has several drawbacks in connection with pattern transfer for microelectronic devices. Most importantly, it is not very selective. Because it is a strictly physical process, the etch rates for different materials do not differ by much. As a result, sputter etching cannot be used in a typical integrated circuit fabrication step, such as etching of contact windows through an SiO_2 film to expose shallow junctions in an underlying silicon substrate, without etching away an unacceptable amount of the junctions. Newer techniques, discussed later on, that rely on both physical and chemical interactions via reactive plasmas are preferable in these applications. However, sputter etching continues to be used where reactive plasmas with suitable chemistries are not known, as in some of the fabrication steps for GaAs, magnetic bubble, and integrated optical devices.

For example, a key step in the fabrication of a magnetic bubble memory chip is the delineation of a pattern of microscopic elements with dimensions on the order of one micron in a magnetic NiFe film with a thickness on the order of half of one micron. Up to 4 million such elements may reside on a chip area of about 1 cm^2. Sputter etching is used by some manufacturers of bubble memories to produce this pattern.

Sputter etching is also useful for cleaning surfaces, particularly for the removal of trace contaminants and thin insulating layers from metal and semiconductor surfaces. In these applications sputter etching usually takes place insitu and just prior to film deposition. A typical application is the deposition of a metal film over an existing metal film or semiconductor surface for the purpose of making an electrical contact. Contaminants or thin interface layers must be removed prior to deposition for acceptably low contact resistance.

Ion Plating

Ion plating, as originally conceived, refers to a technique in which an evaporant stream is condensed on a substrate which serves as the cathode in a dc discharge, typically in Ar (Figure 7-2) [8]. The evaporant atoms (molecules) pass through the plasma in transit, and some of them are ionized. The ionized evaporant atoms are accelerated into the substrate by the applied potential and become implanted in and intermixed with near-surface regions of the substrate, forming a graded interface. This effect leads to superior adhesion and the possibility of forming novel, nonequilibrium "alloys" in the intermixed region.
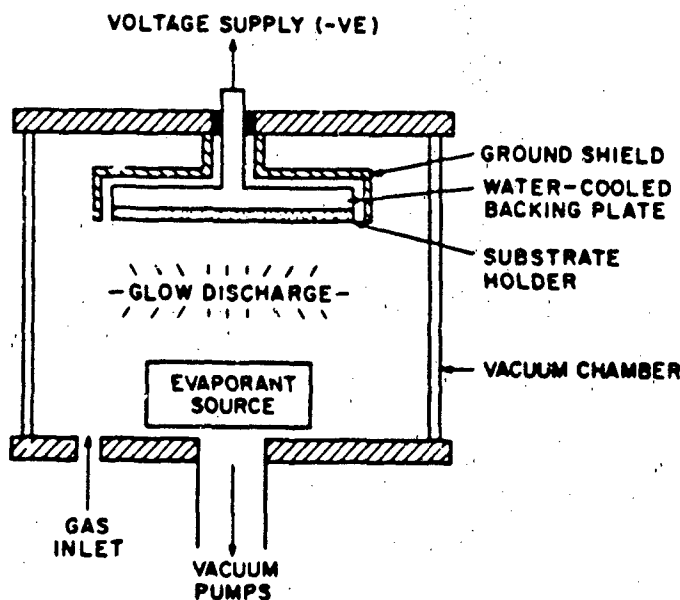
FIGURE 7-2 Cross section of an ion plating system.

Simultaneously, the condensing film is sputter-etched, primarily by argon ions, and some of the sputtered material redeposits on adjacent areas of the substrate that may be shielded from the evaporant beam. The net effect of this simultaneous deposition and etching is a high degree of coating uniformity and "throwing power."

A successful commercial application is the McDonnell Douglas process called "Invadizing" [9]. The process uses ion plating to deposit a dense, adherent coating of aluminum on metal aircraft components to protect them from corrosion. Ion plating has also led to a new class of alloy coatings for gas turbine components that have the composition MCrAlY, where M can be almost any element. Similar applications, targeted at protection against wear and corrosion, are found in the electrical connector and fastener industries.

A broader definition of ion plating, advocated by some, includes any film deposition process in which energetic ions bombard the substrate surface during deposition. A subset of this definition is bias sputtering, where a film is sputter-deposited on a substrate that is externally biased with respect to the plasma to promote bombardment by low-energy ions. This results in a continuous process of sputter deposition and sputter etching at the substrate that is useful in reducing the impurity content of the deposited film, as well as in obtaining better coverage of surface topography. An illustrative application of this technique is the formation of so-called "Ti-gold" for coating jewelry. The deposited film is actually titanium nitride. The optical properties of this material impart a distinctive golden color to films of appropriate thickness and purity. The proper color is much easier to obtain if the deposited films are free of oxygen contamination from background gases.

Most films deposited by sputtering or evaporation have a built-in (intrinsic) stress. Built-in stress can limit the practical thickness of a deposited film because the integrated stress results in shear forces that ultimately overcome adhesive forces and produce delamination. It has been observed that the sign (tensile or compressive) and magnitude of built-in stress can be altered when deposited films are simultaneously bombarded by low-energy ions. This approach allows the deposition of thick coatings of chromium, for example. Similarly, the microstructure and/or stoichiometry of films can be altered by simultaneous ion bombardment during deposition.

Two phenomena of importance in ion plating, sputter etching and ionization in a glow discharge, are relatively well-understood. However, the mechanisms by which simultaneous ion bombardment influences film properties and characteristics, such as stress, stoichiometry, and microstructure, are not adequately known.

Plasma-Enhanced CVD and Polymerization [10]

The high energies of free electrons in a glow discharge result in impact dissociation of molecular gases. The by-products of dissociation include highly reactive molecular fragments and atoms that readily combine on substrates to form thin solid films. An example, germane to the integrated circuit industry, is the formation of SiN films from plasmas formed in mixtures of SiH_4 and NH_3 or SiH_4 and N_2. Such films can be deposited

at rates of several hundred angstroms per minute at temperatures as low as $250^{\circ}C$. In contrast, thermally-induced reactions between SiH_4 and NH_3 require temperatures in excess of $\sim 700^{\circ}C$ to produce SiN. Lower temperatures are desirable to prevent diffusion of shallow junctions and interdiffusion or degradation of metals in silicon integrated circuits.

Polymer deposition can be accomplished with molecular gas plasmas whose parent molecules contain polymerizable structures, such as olefinic double bonds, triple bonds, or cyclic structures. Polymerization is triggered by the formation of reactive species via electron impact dissociation of the parent molecule.

The homogeneity, uniformity, quality, and properties (physical, chemical, and electrical) of plasma-deposited films, whether organic or inorganic, are sensitive to a bewildering number of process variables, such as power, frequency, pressure, flow rate, gas composition, substrate temperature, and reactor geometry, to name only the more obvious. The level of understanding of the effects of these variables is not sufficient for even qualitative predictions to be made. No models of plasma deposition that explain the effects of process variables on film properties have been formulated. Consequently, deposition conditions must be optimized by lengthy and laborious experimentation, and transfer of a process from one apparatus to another is almost never straightforward.

Despite these difficulties, the advantages of plasma deposition, particularly the capability to form films at low temperatures or with unique compositions, have made this approach attractive in several important technologies. Application to integrated circuits has already been mentioned. Plasma deposition as a technique for depositing silicon nitride passivation layers is a routine production process in most of the world's integrated circuit fabrication facilities. Two types of equipment are used in this application. Radial flow reactors (Figure 7-3) were developed first in the early 1970's. More recently, longitudinal reactors (Figure 7-4) resembling "hot wall" low pressure chemical vapor deposition systems have come into use. As might be expected, there is considerable controversy among equipment manufacturers as to the relative merits of each type of system, but neither system appears to have achieved a predominant position among users thus far.

Other integrated circuit applications for plasma deposition, in limited use or under exploration, include the deposition of silicon dioxide, refractory metal silicide, and aluminum films. Competitive techniques, such as physical vapor deposition (evaporation, sputtering, etc.) and low-pressure chemical vapor deposition, may be difficult to displace in these applications because deposition can be accomplished at acceptably low temperatures.

Plasma deposition of inorganic films, such as silicon nitride and silicon dioxide, is also used in other solid-state device technologies, such as GaAs, optoelectronics, and magnetic bubbles. Applications here are primarily for dielectric isolation and passivation.

Another area attracting considerable interest is the plasma deposition of an amorphous form of hydrogenated silicon from a silane plasma for solar cells [11]. This process has potential for developing into a very large industry.
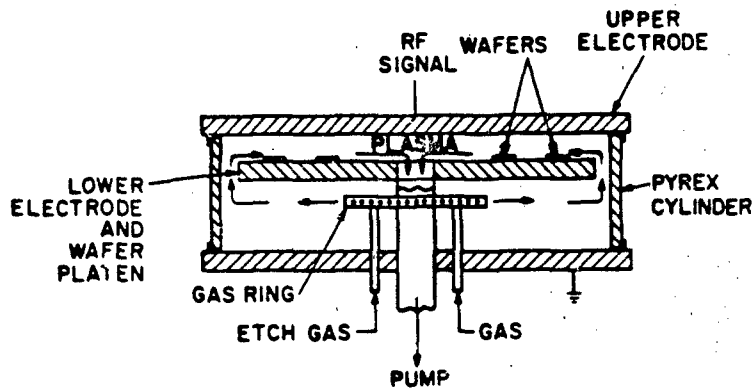
FIGURE 7-3 Cross section of a radial flow reactor.
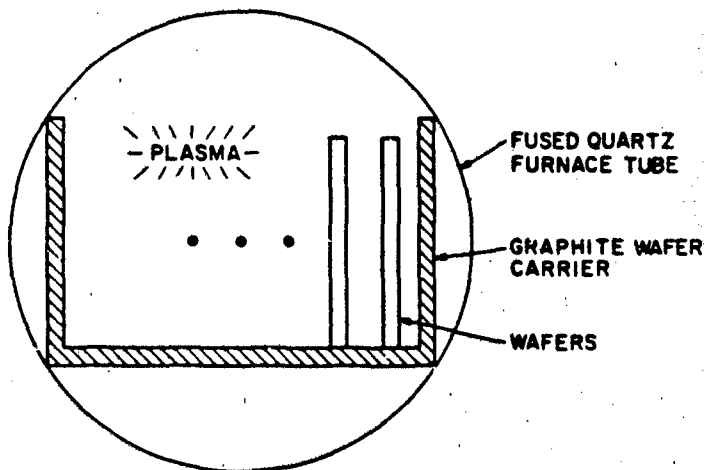
FIGURE 7-4 Cross section of a longitudinal reactor.

The hydrogen incorporated in these films during deposition plays an important role in establishing desirable photovoltaic properties. Numerous Japanese companies have been active in this area. Reported efficiencies have been as high as 10 percent for laboratory devices, but 6 percent for manufactured products is probably a more accurate representation of the state-of-the-art. Solar-powered calculators and watches are among the early products. There is also interest in plasma-deposited amorphous silicon for xerographic and vidicon applications.

Applications for plasma-deposited polymer films appear to be more limited than for inorganic films. Although these films cover substrate topography

reasonably well and can be deposited free of defects and pinholes, even when quite thin, they are generally not mechanically robust and are often semipermeable to environmental contaminants. These shortcomings, together with alternative methods of deposition, may explain the limited application. RCA uses a plasma-deposited styrene film as a capacitive pick-up in its video-disc systems. Plasma polymerized films with low dielectric constants are under exploration for use in integrated circuits as interlevel dielectrics. The low dielectric constants attainable with polymer films are potentially advantageous in reducing parasitic capacitance.

In a quite different area of application, corona discharges are used to modify the surfaces of textiles, effectively functionalizing surface groups in preparation for surface graft polymerization. The grafting can be done by exposing the treated surface to an appropriate plasma containing an effective monomer. Such treatments can be used to change the wettability of the textile surface or to change its printing or dyeing properties.

Polymer membranes for gas separation and water purification can also be formed by plasma deposition, and there are potential applications to biomedical materials.

Plasma-Assisted Etching

In plasma-assisted etching a molecular gas plasma serves as a source of reactive radicals capable of chemically combining with a solid surface to form a volatile product readily removed by pumping. Silicon, for example, can be etched in a CF_4 discharge with gaseous SiF_4 as a by-product. The essential chemical reaction is with fluorine atoms generated in the plasma by electron impact dissociation of CF_4 molecules. The development of plasma-assisted etching has been motivated primarily by the needs of silicon integrated circuit technology.

Various methods of implementing plasma-assisted etching have been devised, leading to a variety of equipment and terminology; plasma etching and reactive ion etching (reactive sputter etching) are the most frequently used terms. The earliest equipment was the barrel reactor (Figure 7-5), a fused quartz cylinder within which an electrodeless rf discharge is maintained. The material to be etched is immersed in the plasma and allowed to float electrically so that only low-energy ions bombard the surface. Etching in barrel systems is isotropic, i.e., the etch rate of a material is independent of direction. Consequently, barrel reactors are not used for critical pattern transfer operations requiring high resolution but are still widely employed for low-resolution etching and plasma stripping of photoresist masks. In 1982, U.S. manufacturers of barrel reactors sold approximately 500 systems at an average price of $30,000 for a gross of approximately $15 million [12].

As the technology evolved, emphasis shifted to parallel electrode systems. In these, the plasma is usually generated by coupling rf power into a gas confined between two parallel electrodes (Figure 7-3) or between a single electrode and a grounded vacuum chamber similar to Figure 7-1. The material to be etched is placed either on the powered or the grounded electrode. The former arrangement is termed reactive ion etching and the latter plasma etching. It soon became apparent that etching in such systems
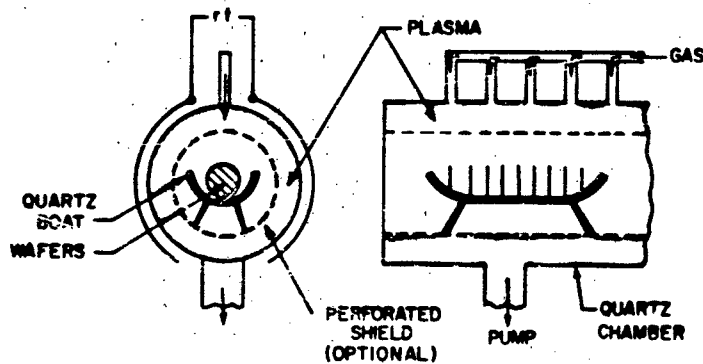
FIGURE 7-5 Barrel reactor.

could be highly directional (anisotropic). Directionality was correlated with the bombardment of the etching surface by energetic ions [13], which, as in sputter etching, impinge on the surface predominantly at normal incidence. The ions are not the primary etchant species but serve, rather, to enhance or even induce reactions between the solid and reactive species generated in the plasma.

Ion-assisted chemical reactions have two important attributes that have had a dramatic impact on integrated circuit technology. First, etch rate anisotropy is attainable. In particular, it is possible to etch through the thickness of a material with essentially no lateral etching. As noted earlier in the discussion of sputter etching, highly anisotropic etching becomes essential for pattern transfer operations as the size of circuit features is scaled down to achieve higher circuit densities and greater performance-to-cost ratios. Second, but of no less importance, because etching occurs through a chemical reaction, etch rate selectivity between different materials can be obtained. This makes possible the patterning of high-aspect-ratio (depth/width) features in a material that overlays a thin layer of dissimilar material without significant removal of the underlying layer. This task must be accomplished several times with critical dimensional control in the fabrication of an integrated circuit. For example, in a state-of-the-art memory device, such as a 256 K dynamic RAM (random access memory), more than a quarter-million bits of information can be stored on a "chip" smaller than a thumbnail. Such a chip may contain some 600,000 circuit elements with minimum dimensions of 1.5 to 2.0 μm that must be controlled to 0.3 μm or better.

The need for high-resolution (anisotropic) etching in integrated circuit fabrication and the unique ability of plasma-assisted etching to provide it has spawned a highly competitive marketplace for plasma etching equipment over the past 5 years. At present there are upwards of 60 companies worldwide either manufacturing equipment for plasma-assisted etching or actively contemplating entry into the market. Because the development of the technology has been largely empirical, available equipment is quite diverse,

with no clearly established preference, as yet. Thus it is entirely likely that there will be additional entries into a market estimated to reach a quarter of a billion dollars by 1986. Ultimately, however, the equipment market probably will be dominated by a few manufacturers.

The explosive growth, pervasive influence, and strategic importance of integrated circuits (IC's) are well known to all. At the present rate of growth, IC sales will reach $50 billion annually by 1990. It is fair to say that today's leading-edge IC products--domestic, Japanese, and European--would not exist without plasma-assisted etching and that continued progress in integrated circuits will be tightly coupled to further development of plasma technology. Further development would be greatly expedited if a better base of understanding was available. As with plasma deposition, a large number of often interdependent variables influence plasma-assisted etching. Despite substantial advances in basic understanding over the past several years, the process complexity still necessitates a largely empirical approach to the development of plasma-assisted etching techniques.

Plasma-assisted etching is also being used or explored for other solid-state device technologies, such as bubble memory, III-V and II-VI compounds, integrated optics, and displays. However, the applications have been more limited and of substantially less economic importance. This is due in part to the limited effort expended. Each of these technologies presents unique problems that must be addressed for the successful application of plasma-assisted etching. For example, in compound semiconductor devices there is an intrinsic difference in reactivity between constituent elements that must be considered. Experience in silicon technology is helpful in providing guidance, but, unless a better base of understanding becomes available, a realization of the true potential for applications of plasma-assisted etching to these and other solid-state device technologies will be won only through hard-fought empirical battles. This implies significant expenditures of time and effort.

Nonetheless, there is ample evidence of considerable promise for plasma-assisted etching in the various technologies listed here. For example, a key problem in the integration of optical sources into a chip technology is that of providing the necessary feedback for the laser structure to reach stimulated emission. One approach that has been pursued is to fabricate a Fabry-Perot resonating cavity by reactive ion etching the mirror faces [14-16].

Another etching application involves the manufacture of multilayer printed circuit boards, which requires the drilling of many small holes. The drilling procedure leaves deposits of organic material which inhibit subsequent plating processes. Removal of these organic deposits from drill holes by exposure to a reactive gas plasma is called "plasma desmearing" and could become a very important manufacturing procedure [17]. Similar plasma techniques are used to remove a wide variety of organic materials from surfaces; the procedure is often called "plasma-ashing."

STATUS OF SCIENCE BASE

The importance of low-pressure plasma processing of materials is apparent even from the foregoing. brief discussion of a few representative

applications. The continued development of these low-pressure plasma processes will have great impact on the competitiveness and progress of high-technology industries (e.g., the semiconductor industry) in the United States. The large amount of money and effort expended toward developing plasma technology justifies, in our opinion, a commensurate effort toward understanding the basic physics and chemistry underlying the technology.

As noted earlier, a reasonable level of understanding is in hand for some of the technologically important processes. But for others, particularly those based on chemically reactive plasmas with applications of growing strategic importance, a dearth of knowledge remains. Plasma-assisted etching is a prime illustration of this assertion. While there have been impressive advances in understanding the basic phenomena governing this technology in the past several years [18], significant technological progress has resulted mainly from "hard-nosed" empiricism. In effect, the science has not yet caught up with the technology, or even pointed the way. This is not an unusual situation; indeed, it is characteristic of much of modern technology development, which tends to be evolutionary. However, many of the roadblocks to successful application of nonequilibrium plasma technology could be ameliorated by expanding fundamental knowledge.

It appears at present that the basic worldwide research effort, is still too small to make any significant impact on the rate of progress. The lack of basic research is partially related to the fact that well-characterized investigations in this field are complicated, time-consuming, expensive, and demand considerable experimental ingenuity; it is also perhaps partially due to insufficient motivation for investigators to enter the field.

The reactions that make glow discharge (cold plasma) processes attractive are often dominated by surface phenomena [19] that occur in a very complicated plasma environment. Moreover, the basic information needed to understand these surface processes is usually unavailable from the plasma experiments. The surfaces exposed to the plasma are uncharacterized with respect to their geometrical structure, chemical composition, and electronic properties. Past experience in surface science suggests that real understanding will not occur until these parameters are defined. Furthermore, the flux and type of species incident upon the surface are almost always unknown. In addition, the flux and energy of ions and/or electrons impinging upon a given surface are usually undefined but are known to strongly influence many reactions [20]. This lack of information forces development of industrial processes primarily on the basis of parameter studies and intuition. This is the state-of-the-art. The plasma reactor parameters that are investigated often include pressure, types of gas or gases, flow rates, residence time, rf power, fixture geometry, fixture materials, the presence or lack of ion bombardment, etc., and often do not lead to a basic understanding of the physics and chemistry. Because of this complexity and lack of understanding, the processes used by industry are quite probably not optimized, and neither is the methodology of process development. Moreover, other useful processes remain undeveloped.

If a body of information were available in a few key areas, this situation would be greatly improved. Some of the key areas involve characterization of the glow discharge, while others are related to particle surface interactions.

Concentration of Particles in a Plasma

Techniques for routinely measuring the concentration of all radicals, ions and stable molecules in a glow discharge are greatly needed. The availability of such techniques would save immense amounts of money in development costs and would also lead to a large increase in knowledge about plasma reactions. Plasma diagnostics using optical techniques, such as laser-induced fluorescence [21-23], optical emission spectroscopy [24], optical absorption spectroscopy [25], actinometry [26], and optical galvanic spectroscopy [27], show some promise of being very useful in this regard. However, quantitative measurements using these optical techniques will require a knowledge of absorption cross sections and the electronic structure of radicals. This information is frequently unknown. Research directed toward obtaining the basic information needed to make them quantitative would be extremely profitable.

The concentrations of particles in a plasma can also be determined with mass spectrometry [13]. Further development of this area would be quite useful, but it probably does not have the same potential for advancing understanding as do the optical techniques.

In any case, a real understanding of surface processes occurring in a plasma will not happen until (among other things) the types and concentrations of species in the gas phase can be determined.

Dissociation in Plasmas

Many plasma reactions are initiated by plasma-induced (i.e., electron-induced) dissociation of stable molecules, and therefore more knowledge of dissociation cross sections and dissociative processes would be valuable. Some information is available [28-35], but much more is needed. Techniques for measuring dissociation cross sections are available, but they are experimentally demanding and time-consuming. Information in this area could be rapidly expanded if competent and interested investigators were available.

Electron Energy Distributions

To make knowledge of dissociation cross sections useful, one must know something about electron energy distributions in a glow discharge. For example, the dissociation rate in a glow discharge is given by [36]

$$G = \int_V \int_E \rho N(E, V)\sigma_d(E)\left[\frac{2E}{m}\right]^{\frac{1}{2}} dEdV \qquad (1)$$

where $N(E,V)$ is the electron energy distribution, $\sigma_d(E)$ the total dissociation cross section, ρ the density of undissociated parent molecules, and V the discharge volume. A 13.56 MHz glow discharge reactor is widely used for a variety of applications; nevertheless, almost nothing is known about the electron energy distributions in these reactors. The authors are aware of only one attempt to model the electron energy distribution [37] in this type

of reactor, and that effort is, at present, unpublished. It is also possible that the work of Garscadden [38] could be extended to model rf discharges. To our knowledge no experimental work is available. The best approach to understanding electron energy distributions in a glow discharge may be theoretical. We suspect (although we are not certain) that application of the theoretical tools developed to understand fusion plasmas (for example, in Tokamaks) or lasers could yield much information if they were applied to the type of glow discharges widely used for industrial purposes.

Plasma Potentials

Processes occurring in a glow discharge often depend quite strongly on the plasma potential or, more correctly on the potential difference between the plasma and a given surface. The potential of the surface is often measured or estimated, but in most applications the plasma potential is unknown. Some basic information on plasma potentials has been published [39,40], but one needs to routinely estimate or measure the plasma potential in the reactor where a given industrial process is being developed. It would he of great advantage to development engineers if a body of basic information were available that would allow an estimate of plasma potentials in a given reactor.

Ion Energy Distribution

There are many synergistic effects in a plasma where ion bombardment enhances a chemical reaction [20]. The magnitude of the synergistic effect depends on the energy of the incident ions. Consequently, a body of information about the energy of ions that collide with surfaces in a plasma reactor would be very valuable. This area is amenable to both experimental and theoretical approaches.

Plasma-Surface Interactions

The final key areas involve plasma-surface interactions. Ideally, one would like to conduct well-defined surface experiments inside a plasma; however, at present this seems to be impossible. Therefore, investigations in these areas should probably be conducted outside the plasmas, where well-characterized molecular beams can be interacted with well-characterized surfaces.

The lack of understanding of plasma-surface interactions is directly attributable to the fact that these surface reactions often involve atoms or other types of radicals and that there are few investigations of the interaction of a well-characterized flux of radicals with a well-defined surface. Moreover, there are synergistic effects in the plasma.

Basic research in four areas of surface science could do much to remedy this lack of information:

- Recombination reactions, i.e., investigation of reactions at a surface where radicals recombine to form stable molecules.

- Investigation of synergistic effects where ion, electron, and photon bombardment change the reaction characteristics of the incident radicals. For example, a knowledge of the dependence of reaction rate constants on the type and energy of bombarding particles would be very useful.

- Investigation of the adsorption characteristics of a number of radicals; these should include a determination of sticking probabilities [41] as a function of surface coverage and conditions.

- Investigation of mechanisms for the conversion of reactants to products in the surface region.

In the case of etching reactions, these experiments could include identification of products on the surface (e.g., by using X-ray photoelectron spectroscopy) and identification of products and measurement of energy distributions of particles entering the gas phase (e.g., by using modulated beam mass spectrometry).

The equipment required for this type of research would probably include a standard UHV system with Auger, LEED, UPS, and XPS capability, as well as the capability for ion and electron bombardment. This capability would be used to characterize the sample surface. In addition, one would need two or more well-characterized molecular beams of radicals directed onto the surface. These molecular beams should be chosen to best simulate a specific plasma of interest. This latter demand is the major experimental problem. It is quite difficult to generate a molecular beam of a given radical that does not contain other radicals or impurities. Nevertheless, it is our opinion that research along the lines suggested could be quite productive, although it would be expensive and would demand considerable ingenuity.

In the following we give a few of the many possible examples of problems that could be resolved in the field of plasma etching, if some of the information described here were available. Similar examples could be given for other nonequilibrium plasma processes, such as plasma deposition, glow discharge sputtering, plasma anodization, and plasma polymerization, but such examples are not necessary to make the point.

Consider a plasma etching process that uses CF_4 (gas). CF_4 itself is quite inert, so the etching reaction results from radicals produced by electron-impact-induced dissociation of CF_4. There are three major dissociative processes in CF_4: dissociative attachment ($CF_4 + e \rightarrow CF_3^- + F$ or to $CF_3 + F^-$), dissociation into neutral fragments (e.g., $CF_4 + e \rightarrow CF_3 + F$) and dissociative ionization (e.g., $e + CF_4 \rightarrow CF_3^+ + F$). The cross section for each of these processes is known or could be estimated. Therefore, if the electron energy distribution was known for a given plasma reactor, then one could determine the dominant dissociative process and hence seek ways to optimize it.

As a second example, the maximum quantity of atomic fluorine available for etching is equal to the dissociation rate "G" given by Equation 1. The efficiency of the discharge process could be estimated by comparing the amount of fluorine incorporated into etch products (e.g., using mass spectrometry)

with the dissociation rate "G." This type of estimate again demands a knowledge of the electron energy distribution and the relevant cross sections.

A third example involves recombination. The importance of recombination reactions (e.g., $CF_3 + F \rightarrow CF_4$) could be estimated by comparing G with the quantity N of CF_4, introduced into the reactor and the quantity N' pumped away. If G >> N, then recombination is very important. If G > (N-N'), then recombination is still important. From a practical point of view, elimination of recombination reactions should increase the etch rate. Knowing how the rate of recombination is influenced by operating parameters would allow better process control.

In other situations it may not be necessary to dissociate the molecule for etching to occur. The interaction of SF_6 with silicon may be an example since it has been shown that vibrationally excited SF_6 will react spontaneously with silicon [42]. Comparison of the dissociation rate with the etch rate could indicate whether dissociation was important for the plasma etching of silicon using SF_6. If the etch rate is much greater than the dissociation rate, then vibrational excitation of SF_6 may be the dominant process that leads to etching.

Although a large number of examples could be given, we will use one example which illustrates the importance of knowing (a) the concentrations of particles in the gas phase, (b) the reaction probabilities of these particles at a surface and (c) the products formed by recombination and etching reactions. Let us consider the etching of SiO_2 in a glow discharge that uses CF_4 (gas). Electron impact dissociation of CF_4 produces primarily CF_3, F and CF_3. Subsequent reactions may produce many other species. A knowledge of rate constants and gas phase concentrations would allow one to estimate whether gas-phase recombination (e.g., $CF_3 + F \rightarrow CF_4$) was a significant loss mechanism for fluorine atoms. A complete lack of information about the gas phase CF_3 concentration presently prohibits this estimate.

An earlier paper [43] speculated that CF_3 radicals would spontaneously etch SiO_2. Many investigators have subsequently made the same suggestion. This speculation led to the development of one of the key processes in the fabrication of very-large scale integrated circuits, the formation of contact windows. Yet, today the true role of CF_3 radicals is still unknown and there has been no persuasive experimental verification of the early speculation. A well-defined experiment needs to be conducted to determine whether this reaction actually happens.

It has been shown conclusively that fluorine atoms react with SiO_2 and that ion and/or electron bombardment greatly enhances the reaction rate. A knowledge of the gas phase concentration of CF_3 and F and of their reaction probabilities (sticking probabilities) at the SiO_2 surface would allow one to determine which particle dominates the etching reaction. The presence of ion bombardment is likely to alter these reaction probabilities, i.e, there is probably a synergistic effect. Synergistic effects have been investigated for fluorine alone but not for CF_3. An investigation of synergistic effects for CF_3 interacting with SiO_2 under ion bombardment would be very enlightening.

The carbon deposited on the SiO_2 surface must eventually leave the surface through an etching or recombination reaction. The products of this reaction are likely to be CO_2, CO, COF_2, or CF_4, or a combination of these molecules. Experiments are needed to determine which of these molecules do indeed leave the SiO_2 surface and how that is affected by ion bombardment. This type of information would also allow one to estimate the fraction of the fluorine adsorbed on the surface that is eventually incorporated into an etch product.

Similar examples of fundamental issues that might profitably be addressed in relation to other applications of nonequilibrium plasmas could be given, particularly where reactive plasmas or synergistic effects are involved. Plasma etching is perhaps the most extensively studied area. The amount of fundamental information available on plasma-enhanced CVD and the growth of films under energetic particle (ion, electron, photon) bombardment is small by comparison. Questions pertaining to the constitution of the plasma and how it determines film composition, morphology, stress, etc., need to be answered before one can hope to minimize the number of parametric adjustments to produce desired film properties.

CONCLUSIONS

There are many questions about basic mechanisms (other than those posed here) in CF_4-Si,SiO_2 plasma etching that remain unanswered despite the fact that these are the most studied etching reactions. Moreover, many different etching gases are used for other materials applications, and similar questions arise for these situations. For example, chlorine-based gases are widely used in the semiconductor industry to etch silicon and aluminum. A plasma process for etching copper and magnetic materials such as nickel and iron is badly needed but presently unavailable. Analogous research is needed for an understanding of plasma polymerization and plasma-enhanced CVD. Therefore, it is certain that basic research directed toward an understanding of relevant plasma reactions will strongly influence future technology development. Basic research in this area is both interesting from a scientific point of view and profitable from an applications point of view. The fields of plasma-enhanced CVD, plasma etching, and plasma polymerization, which involve very complex chemistry, are to be contrasted with the fields of glow-discharge sputtering, surface modification, surface cleaning, etc., which involve more physical processes. In the latter cases, extensive basic research may not be pivotal to continued development.

Real advances in the understanding of the plasma processes mentioned require the development of new experimental methods or application of sophisticated techniques from other scientific areas. This situation is reminiscent of the field of surface science in the late 1960's and early 1970's, when the development of "low-energy electron diffraction," "Auger spectroscopy," X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, X-ray extended fine structure spectroscopy, etc., led to a dramatic increase in basic knowledge and had a powerful impact on the development of technologies that hinged on surface phenomena. Financial support for basic research would probably be most effective if given to investigators who are willing to apply new techniques or else to apply tools from the fields of surface science, atomic physics, and lasers (or other

optical techniques) to the field of plasmas. In our opinion, support for research based on parameter studies is not as expeditious unless directed toward the specific development of a product or process.

Finally, the number of experimental parameters that influence the operating characteristics of a plasma processing system is very large. A body of basic information, such as that described above, is needed so that qualitative or semiquantitative estimates can be used to determine the dominant parameters for a particular application. It is not necessary to have a quantitative understanding of the physics and chemistry of each plasma processing system, but it is important to have a qualitative understanding of the composition of the plasma, the reactions that are occurring, and the effect of parametric variations on these. Such information would provide at least a modicum of predictability and perhaps a more rational basis for process development.

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CHAPTER 8

TECHNOLOGICAL OPPORTUNITIES

A crucial purpose of this report is to provide a current and critical assessment of plasma processing, with emphasis on the technological opportunities as defined by both the technical feasibility and the economic incentive, together with the critical R&D needs to attain these goals.

The material presented here is divided according to the subjects presented in the previous chapters. Process description, summary of current status, technological opportunities, and critical R&D needs are identified for each subject.

THERMAL PLASMA MELTING AND REMELTING

Process Description

A thermal plasma heat source is characterized by a high concentration of energy and associated high gas temperature. The melting and refining of primary metals, the remelting of specialty alloys and reactive metals, and metal scrap melting represent the dominant industrial processes. Thermal plasma reactors and associated techniques for melting, remelting, and processing materials have distinct advantages over competing technologies. These advantages include the ability to achieve a controlled steady-state uniform flow of partially ionized gas with bulk gas temperatures well above those obtained with chemical flames, combustion, or resistance heater systems; complete control of the atmosphere by operating in an inert or reactive environment, thus also aiding in reducing exhaust pollution; operation at elevated pressures with inert gases to minimize the loss of high-vapor-pressure constituents while also eliminating the need for expensive vacuum pumping equipment; steady-state operation at reduced voltage fluctuations; high material melting rate and heat addition (superheat) to the molten material with variable reaction times attainable independent of the electrode feed rate; and availability of nonconsumable electrodes to minimize melt contamination. In addition, thermal plasma reactors are compact systems that can process material in a variety of forms (e.g., solids, chips, powder) at high throughput rates and with relatively high electrical and thermal efficiency. Thermal plasma reactors also have the potential to produce new materials and products not defined at this time.

Summary of Current Status

In an era of growing awareness that conservation of materials must be pursued in an efficient and cost-effective manner, new thermal plasma processing techniques are being considered throughout the metals processing industry in converting the raw material into ingot-type products. With only a few exceptions (e.g., plasma spray torches and plasma welding equipment), thermal plasma melting technology in the United States is still in the laboratory or pilot-plant stage. In comparison, foreign countries have a variety of full-scale production systems in continuous operation that meet the stringent requirements of high throughput, reliability, efficient utilization, and good return on investment. Examination of the accumulated data base shows that Japan, the Soviet Union and the German Democratic Republic are taking leadership roles in pioneering operation of large-scale plasma reactor systems, with steady-state power levels exceeding 20 Mw, for melting applications. Based on the examples described in this report, a reasonable level of technical understanding is available for several of the important thermal plasma melting reactor systems. A prime example is the new developments using the plasma progressive casting/cold crucible reactor for providing efficient processing and recycling of scrap and alloy materials, thus serving to conserve both hydrocarbon fuels and critical materials. Plasma processing for melting applications can also play a dominant role in the increased electrification of U.S. industry.

Technological Opportunities

The melting and processing of many metals and alloys is particularly energy-intensive; therefore, as the United States shifts more toward electricity as the major energy base, numerous high-temperature plasma material processing applications will result.

Worldwide, industrial furnaces of all types consume about 50 percent of the energy resources provided in the world, and thus the impact of converting even a small percentage of these furnaces to efficient thermal plasma reactor types is very significant.

The following is a list of key technological opportunities for thermal plasma melting technology.

- Cold crucible melting and recycling of strategic scrap material using continuous ingot withdrawal techniques, including melting metals and alloy scrap in the form of solids, turnings, and powders into a dense, reusable ingot within physical and chemical specifications.

- Consolidation, alloying, and blending of nonstrategic scrap into bulk weldable electrodes as used in secondary vacuum arc remelting.

- Casting production of reactive and volatile metals and alloys and preparation of alloy master melts.

- Production of large monocrystals of refractory metals, directionally solidified eutectic alloys, and high-melting-point carbides.

- Production of ultraclean superalloy powders as used in aerospace applications; production of new refractory powders for high-temperature ceramic applications.

- Reprocessing nuclear wastes for volume reduction and stabilization of the noncombustible solid waste.

- Toxic chemical waste treatment and decomposition of hazardous waste into simple compounds for subsequent scrubber or flare treatment.

- Production of nitrogen-alloyed steels via a plasma injection technique as a substitute for chrome steels.

- Ingot casting and slab surface preparation and treatment prior to secondary grinding processing.

Critical Research and Development Needs

The successful design of future production-scale thermal plasma reactors for melting and material processing applications will require a broad understanding of the reaction kinetics, transport properties, particle dynamics, and heat transfer aspects of very-high-temperature multiparticle systems. Significant progress in thermal plasma processing has been impeded by a lack of basic understanding of the physics and chemistry of gas-solid, gas-gas, and solid-solid interactions within the plasma reactor. Research in thermal plasma melting technology to date has been strongly oriented toward technical feasibility studies for the development of a specific process (in many cases proprietary, unpublished information).

The majority of the basic R&D studies appearing in the literature have been made on plasma welding and cutting technology. There is a need for basic research to close the existing gap between the fundamentals of thermal plasma technology and the physics and chemistry of process metallurgy. An interdisciplinary approach will be required to further the understanding of this complex but most important technology. With this type of approach, before the end of this century we may see the manufacture of basic products such as steel, fertilizer, silicon, acetylene, cement, and new superalloys benefiting from large-scale developments in plasma technology.

The following examples describe the fundamental long-range research needs for thermal plasma melting technology.

- Investigation of nondeteriorating (nonconsumbale) electrodes capable of steady-state long-lifetime operation at high current levels. Included should be determination of critical failure mode, the effects of electrode design, composition, and cooling on electrode performance and lifetime, and the effects of key operating parameters on electrode erosion. This information will eliminate cross-contamination and process downtime.

- Improved systems for introducing, in a continuous and reproducible manner, controlled amounts of feedstock to be melted and processed. This includes studies of the physical interaction of materials (solids, chips, powders)

injected into and entrained in the plasma discharge and molten pool interface region and potential advantages of pretreatment and preheating of feedstock, as well as improved quench techniques to permit efficient product separation.

- Fluid dynamics and thermal modeling of the plasma system. Emphasis should be on mathematical models for gas flow field, electromagnetic force field, and temperature field in dc transferred arc mode plasma systems, and on modeling of the molten-ingot-crucible interface heat transfer and macroflows within the molten pool.

- Determination of the physical limitations to high throughput of material. This includes the feeder systems, plasma heat source, hearth or crucible, and ingot withdrawal system. Optimization of the system should be sought for maximum ingot withdrawal rate combined with improved techniques for achieving completely dense, homogeneous final ingots with minimum erosion and contamination and with good surface finish.

- Investigation of new techniques for complete removal of inclusions (low and high density) from processed material. This should include the use of material pretreatment, cleaning, segregation schemes, and hearths for settling or floating out deleterious material, as well as determination of trace element buildup resulting from increased utilization of recycled materials.

- Investigation of absorption and desorption of plasma species by metal melts, including determination of reaction mechanisms and rate coefficients. Also included should be secondary refining processes for decarburization, deoxidation, and alloy additions involving combination of injection metallurgy techniques with a thermal plasma-heated carrier gas.

- Identification of key parameters for achieving clean melts, fine grain size, and improved microstructure of dense ingots. This includes investigation of effects of plasma discharge heat flux distribution, prescribed discharge motion on molten pool, influence of external magnetic fields on mixing, and heat transfer losses to mold and crucible systems.

- Establishment of new techniques for material pretreatment and contamination identification and removal. Included here are both passive and active diagnostic systems for on-line identification of elemental constituents, contamination, and distribution of contamination (surface or bulk) input feedstock. Novel combined chemical-plasma techniques for contamination removal from strategic materials should also be investigated.

- Investigation of physical metallurgy of thermal plasma surface treatment and glazing. This includes characterization of different plasma modes (i.e., transferred, nontransferred) relative to local surface melt efficiency and heat transfer losses as well as determination of operating parameters for optimized workpiece surface treatment and maximum processing rate.

- Modeling development to permit scaling from laboratory-size thermal plasma melting reactors (typical 5-cm-diameter ingots) to production-size plasma reactors (typical 45-cm-diameter ingots or slabs). This should include detailed heat transfer analysis and sensitivity analysis to variations in operating conditions.

The following examples describe critical development needs and engineering studies required in thermal plasma melting technology.

- Establishment of pilot-plant-scale demonstration equipment and full-scale production hardware optimized for a specific application so as to provide highest product yield at minimum cost. This includes optimization of feedstock form and throughput, plasma source configuration and operating mode, on-line diagnostics for monitoring input material, contamination limits and quality of the final product relative to specification, as well as possible interface with current automated computer-controlled feedback and control systems and robotics.

- Detailed economic analysis of several selected technically feasible thermal plasma processing systems. This should include sensitivity analysis of raw material costs, electrical costs, equipment utilization, overall efficiency, and related considerations.

- Detailed engineering evaluation of thermal plasma melting systems relative to alternative competing technologies (e.g., vacuum arc remelt, electron-beam, plasma beam, electroslag remelt).

PLASMA EXTRACTIVE METALLURGY

Process Description

Extractive metallurgy is winning metals in their pure or usable alloy form from ores. Extraction and refining occur at temperatures ranging from 1273 to 1773 K. When the required temperatures exceed 1673 K the use of electrical energy is generally the only efficient way to carry out the extraction process. Chemical reactors that use thermal plasmas as the energy source are logical candidates for such processes. The concentrated elevated-temperature heat source of the plasma furnace permits high rates of metal production per unit volume when designed to fit the thermodynamic equilibria, kinetics, and required heat transfer of the reactions in question.

Summary of Current Status

The technical promise of plasma reactors for use in extracting metals from ores is well established. No full-scale commercial installations are documented in the open literature; however, with few exceptions, applications of high-temperature plasma reactors to extractive metallurgy are still under laboratory, pilot-plant, or demonstration-plant development. One reason for this is that the 20 to 100-MW plasma torches required for economic production are still in the development stage and are not yet commercially available (see Ref. 27 of Chapter 4).

Some important extractive process applications in the advanced stages of development are the following:

- Recent advances in the design of transferred arc plasma reactors in the German Democratic Republic and the Soviet Union have resulted in demonstration commercial plasma furnace installations of 10 to 20-MW capacity (using multiple plasma torches of 3.0 to 3.5-MW) in ferroalloy production and steel processing (see Ref. 1 of Chapter 4). Similar applications are under consideration in North America (see Ref. 51 of Chapter 4).

- A 70,000-ton per year, $26 million plant for the plasma recovery of metals from precipitator dusts is under construction in Landskrona, Sweden (see Ref. 24 of Chapter 4).

- Plasma heating of air blasts and injected fuel has been demonstrated to increase productivity and reduce coke requirements in iron blast furnaces (see Ref. 37 of Chapter 4).

Technological Opportunities

Although its current use is limited, plasma technology offers interesting opportunities for processing difficult-to-reduce or high-melting point metallic materials, or for the production of metallic materials where the current technology is complex or expensive. Whether this technology will be economically attractive depends on the volume of materials, national strategic importance, electrical energy costs, the solution of some difficult engineering problems, and the cost of scrapping existing equipment. When these criteria are applied, it appears that this technology will be used for primary reduction of zinc, titanium, molybdenum, cobalt, nickel, and tungsten ores in 5 to 10 years using 10 to 20-MW torches.

The major long term (10 to 20 years requiring 20 to 100-MW torches) advantage, however, may be the direct reduction of lean domestic ores and wastes (such as fly ash) to produce aluminum, ferrosilicon, titanium, electric power, and by-product carbon monoxide. This would be carried out as an integrated processing complex using plasma technology for the more difficult separations, in which all wastes are consumed as raw materials for other processes. In principle, 100 million tons of fly ash per year resulting from coal burning could provide a substitute source for all of the aluminum consumed in the United States, 40 percent of the iron ore imported, and all imported ferrosilicon, while providing carbon monoxide for organic synthesis or clean power generation. Such a system could solve most of the problems besetting the metallurgical industry today.

Critical Research and Development Needs

The physical and chemical phenomena of plasma processes are poorly understood. If the technological opportunities mentioned are to be realized, generalized design criteria must be developed to avoid the present waste process of trial and error in reactor design; fundamental knowledge must be developed that relates the properties of the plasma state to the thermodynamic, kinetic, and heat transfer requirements of the reactions of

process metallurgy. Furthermore, engineering design problems, the solutions of which are necessary to translate these findings to commercial application, must be attacked.

Critical research and development needs, then, may be divided into fundamental understanding and engineering studies.

Fundamental Understanding

To estimate the technical and economic feasibility of proposed plasma processes and to design efficient reactors it is necessary to predict chemical reaction mechanisms, develop mathematical models, and estimate the effect of plasma furnace design.

- Chemical reactions in the plasma state are not well understood. Electrons, positive and negative ions, and radicals interact by both chemical and physical processes with injected particulate reactants. Spectroscopic or other means of identification of the chemical species present during reaction as a function of temperature, pressure, and feed composition must be developed if the gaseous and solid feed ratios necessary to obtain the desired products are to be determined.

- Mathematical modeling to develop a generalized set of equations for process engineering design requires knowledge of thermodynamic and transport properties and of heat transfer mechanisms. The effect of fluid flow patterns and velocities, temperature, residence time, and other forms of energy on the reaction rates must also be known. Sensors and diagnostic tools must be developed to determine these parameters.

- The effect of plasma furnace design on the reaction rate model must also be determined. Furnace design includes the selection of transferred or nontransferred arc, alternating or direct current, and means of increasing reactant residence time by mechanical or electrical arc expansion or entrapment in a falling film or pool of product.

The necessary fundamental investigations could best be carried out at two or three university centers equipped to develop the diagnostic techniques and make the measurements necessary to develop the needed design data base.

Engineering Studies

Significant engineering problems already identified that must be solved may be divided into three parts--engineering design, materials of construction, and conceptual flow sheet analysis.

- Engineering design must concentrate on increasing reactant residence time and removing heat for rapid quenching of products (to avoid back-reaction) while efficiently returning the energy removed to the process if viable commercial application of this technology is to be achieved. Equipment for reliable feeding of finely divided reactants at the proper location and in a manner necessary for rapid reaction, equipment for the removal of products, and the design of reactors tolerant of circuit interruption and switching are necessary.

- It will be necessary to develop reliable materials of construction extending reactor lining and electrode life for the reduction of downtime and economic exploitation of the technological opportunities listed.

- High power costs and abundant fossil fuel make new electrical processes marginally advantageous in the United States, and plasma technology will have only economic application in specialized areas. These must be identified by engineering studies of conceptual processes.

The engineering design problems are best studied in the laboratories of the industries where plasma technology can be calculated to show an economic advantage. If through government support the necessary fundamental information is made available and conceptual studies identifying applications that promise good return on capital investment are made, the industries identified as the most likely candidates can be counted on to commercialize these profitable processes in their own laboratories.

PLASMA DEPOSITION PROCESSING

Process Description

In plasma deposition processing, a high intensity plasma flame is utilized for melting and consolidating pre-alloyed powder feed onto the workpiece surface. Plasma spraying involves injection of the powder particles into the high velocity plasma jet stream, where they undergo rapid melting, and acceleration toward the workpiece surface. Rapid quenching occurs when the molten particles collide with the substrate and build-up the deposit. In conventional plasma spraying, the workpiece is usually protected from environmental interactions by a shroud of inert gas, whereas in vacuum plasma spraying, the entire system is enclosed in an evacuated chamber, which is maintained at about 30 to 60 torr inert gas pressure. Plasma transferred arc deposition is essentially a weld overlay process, in which the source of alloying material is a continuous stream of pre-alloyed powder. Normally the plasma jet induces some surface melting of the substrate so that the powder feed forms an overlay deposit that is fused to the substrate.

Summary of Current Status

Plasma sprayed deposits have been used as protective coatings in corrosion and wear applications and as high-thermal-flux barriers. Deposits have also been used for building up worn bearing surfaces and for making thin-walled structures. With the advent of vacuum plasma spraying, quality coatings of high-performance materials have become available, that are already finding useful application in industrial gas turbines and jet engines.

Many types of deposits have been produced by conventional plasma spraying, including refractory metals (W, Ta, Mo), carbides (Cr_3C_2, WC, TaC), borides (TiB_2, ZrB_2), oxides (Al_2O_3, Y_2O_3, TiO_2), intermetallics (Cr_3Si_2, $MoSi_2$), and mixed phases (Y_2O_3/ZrO_3, WC/Co). Advanced coatings of the MCrAlY type (M = Ni, Co, Fe, Ni/Co) and high-performance Ni- and Co-base superalloys have also been produced by vacuum plasma spraying.

Plasma transferred arc deposition has been widely used as a hardfacing treatment for many years, and new applications continue to be found. The range of applications may be increasing because of the ability now to create novel composites (e.g., TiC particle dispersions in conventional alloy matrices) using mixed powder feeds.

Technological Opportunities

Historically, research and development in plasma deposition technologies has been concerned primarily with gun (torch) designs, particle injection techniques, environmental controls, and structure-properties-process interactions. There is little doubt that continuing research and development along these lines are needed to further optimize plasma deposition technology. In addition, it seems appropriate to augment such activities with initiatives that are targeted to specific problems of high potential pay-off, such as the following:

- Rapidly solidified amorphous or microcrystalline coatings, thin shell structures, and monolithic, near-net shapes.

- Graded structures by alternating powder feeds or multiple guns.

- Novel coatings by combined plasma and CVD processing, utilizing organometallic precursors.

- Composite hardfacing materials by advanced powder mixing and gas injection techniques.

- Higher energy density focused plasmas to compete with lasers in rapid solidification surface treatments.

- Fast response sensors, integrated with computer-controlled systems (robotics).

- Underwater plasma spraying capabilities for marine applications.

- Post deposition thermomechanical treatments for improved surface properties.

- Dispersion-strengthened deposits by displacement reaction processing.

Critical Research and Development Needs

Plasma deposition is a very complex process requiring the control of many variables to produce high-quality deposits. The critical variables are those connected with particle/plasma (melting) and droplet/substrate (solidification) interactions. The critical research and development needs in these areas are as follows:

- Better understanding of the characteristics of the plasma jet, including temperature and jet velocity profiles.

- Modeling of particle trajectories and determination of dwell time in order to establish the characteristics of the melting process.

- Improved diagnostic techniques to measure particle trajectories, plasma jet temperature and velocity profiles.

- In vacuum plasma spraying, determination of the effect of the shock wave developed ahead of the gun on the jet character, and the mechanics of momentum and heat transfer to particles in the plasma jet.

- Modeling and experimental evaluation of droplet splatting kinetics and subsequent solidification.

THERMAL PLASMA SYNTHESIS AND CONSOLIDATION

Process Description

In general, thermal plasmas lend themselves to synthesis and consolidation of refractory materials which require high-temperature and contamination-free environments (no combustion products). Materials injected into thermal plasmas receive higher rates of heating and may reach substantially higher temperatures than are obtained with conventional processes. Extremely fast rates of product quenching are also readily accomplished. These unique features of thermal plasmas enable, for example, the synthesis of new materials (metastable phases) which are very difficult or impossible with conventional techniques. The production of a metastable tungsten carbide phase (WC_{1-x}) is one such interesting example (see Ref. 51 of Chapter 5).

Summary of Current Status

The preparation and processing of metal and ceramic powders and their mixtures by thermal plasmas are practiced commercially in a limited number of instances. The preparation of submicron ceramic particles of SiC, Si_3N_4 and a number of the oxides are important examples of plasma synthesis. These powders, especially silicon carbide and nitride, may be useful for the preparation of high performance ceramic bodies. The spheroidization and densification of powders and presintered conglomerates and the preparation of high purity materials are also current applications.

Technological Opportunities

The most important opportunities for thermal plasma synthesis and consolidation include:

- Production of submicron oxide powders (e.g, TiO_2, ZrO_2, SiO_2). Such powders have a wide range of uses including surface casting, high density ceramics, pigments, catalysis, and dispersion strengthening of metals.

- Synthesis of ternary carbides and nitrides from the elements or by direct reduction of the oxides and simultaneous synthesis of the carbides.

- Oxide reduction and alloying in one processing step, a technology which has been little explored.

- Thermal plasma dissociation of compounds (e.g., zircon sand for making zirconia).

- Spheroidization and densification of porous particles and conglomerates.

- Plasma sintering, in particular, of ceramic materials.

Critical Research and Development Needs

Since thermal plasma synthesis and consolidation is a rather new discipline, it is not surprising that the science base is poor. Most reported work has relied heavily on intuition and trial and error methods. The basic and development needs of various parts of this technology include:

Synthesis and Consolidation Equipment

- Studies of electrode heat transfer, specific heat fluxes, and electrode erosion.

- Plasma reaction modeling and establishment of scaling laws.

- Optimization of reactors for specific processes.

- Development of pilot plant and scale-up of plasma reactors.

Gas and Particulate Injection into Plasmas

- Temperature and velocity fields in plasmas and their parameter dependence.

- Plasma transport properties (mixtures).

- Deviation from local thermodynamic equilibrium.

- Interaction of injected cold gases with plasmas; effect of chemical reactions.

- Plasma/particulate interaction; heat and momentum transfer; melting and evaporation; Knudsen effect.

- Particule nucleation from the vapor phase (homogeneous, heterogeneous).

- Development of handling systems for chemically aggressive starting materials.

- Improvement of particle feeders; scale-up of laboratory feeders.

Submicron Particle Synthesis

- Studies of particle formation and particle growth.

- Effect of quench rate on particle size and size distribution.

  Development of full-scale, economical collection and separation equipment for contamination-sensitive products.

Plasma Dissociated, Spheroidized and Densified Materials

- In addition to previously cited needs, the plasma sintering process requires basic heat transfer studies in plasmas which deviate substantially from local thermodynamic equilibrium.

PROCESSING OF MATERIALS USING LOW-PRESSURE, NONEQUILIBRIUM PLASMAS

Process Description

Low-pressure, nonequilibrium plasmas are used for a variety of processes such as plasma-assisted etching, plasma-assisted chemical vapor deposition, plasma polymerization, glow discharge sputtering, surface cleaning, and surface-modification. These plasmas provide a unique environment where high energy electrons exist in an otherwise "cold" gas. This permits preparation, processing, and modification of materials at lower temperatures than are possible by more conventional means. Such plasmas can also be used to generate a large flux of highly energetic species (e.g., ions) at a surface of interest. Unique chemical environments are also obtained using this type of plasma. The applications are many and diverse; a more detailed description of the processes is given in Chapter 7.

Summary of Current Status

The use of nonequilibrium plasmas for materials processing in manufacturing and laboratory situations is growing rapidly, particularly in strategically and economically important areas such as solid-state device fabrication. A particularly noteworthy example is in the processing of very-large-scale integrated circuits (VLSIC) where plasma processing is presently a critical, indispensable part of the process technology.

Technological Opportunities

The trend of expanding applications in solid-state device fabrication will continue. The major growth area would appear to be in the application of reactive plasmas, especially for plasma-assisted etching and plasma-enhanced CVD.

Because reactive plasmas represent the least understood facet of nonequilibrium plasmas, they offer the promise of uncovering many new and attractive applications that our lack of knowledge makes difficult to forecast. Clearly, however, timely development of new applications as well as optimization of processes for present applications will depend on the rate of acquisition of the necessary knowledge and understanding.

There are technological opportunities in many fields that use low-pressure plasmas. The examples given here, in our opinion, offer possibilities for the greatest economic gain and/or are strategically most significant.

Plasma-Assisted Etching

- Continued development of this technology for VLSIC is vital if higher density circuits are to be realized.

- Application to technologically important materials where no viable reactive plasma technology presently exists, such as the etching of copper, aluminum-copper alloys, magnetic metals (e.g., nickel, cobalt, iron, and their alloys), and noble metals (e.g., gold, platinum, and palladium), should be pursued actively.

- Intensified development of techniques applicable to compound semiconductors and materials for integrated optics and projection-type displays is imperative.

Plasma-Enhanced CVD

- Continued development of techniques to produce high-efficiency, hydrogenated amorphous silicon for solar energy conversion and other photovoltaic applications (e.g., as a photoconductor for xerography) is important.

- Extension of these techniques to compound semiconductor and photonic devices where low-temperature processing is required could have a significant pay-off.

- Development of novel materials with unique characteristics should be sought. For example, many polymers formed by plasma polymerization have properties and characteristics that are very useful but are quite unlike polymers formed by conventional techniques.

Critical Research and Development Needs

The research and development needs for nonequilibrium plasmas can be divided into applied research and engineering directed toward the development of a specific process and/or product, and basic research that is aimed at providing information and understanding that is generally applicable to a variety of situations.

Government support of basic research is probably essential if the work is to be accomplished expeditiously and made available to all segments of industry. In contrast, industry is developing or has developed a large number of plasma-related processes and products. In the absence of strategic considerations (e.g., for national defense), government support in this area may not be essential.

Basic Research Needs

Basic research needs fall mainly in the areas of plasma-assisted etching, plasma-enhanced CVD, and plasma polymerization that involve complex chemistry. These are to be contrasted to applications that mainly involve physical sputtering, where basic research may not be pivotal. Nevertheless,

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it should be emphasized that, because of similarities in the plasma
environment, research on reactive plasmas will yield information applicable to
more physical plasma processes.

The basic needs fall in three general areas. These are listed here
together with some specific approaches to meeting those needs.

- Characterization and understanding of the plasma environment.

  -Development of techniques to determine the chemical composition of
  plasma and to relate the composition to plasma parameters subject to
  control.

  -Characterization of the energy distributions of ions, electrons, and
  neutrals in the plasma.

  -Acquisition of information pertaining to excitation and dissociation
  of molecules.

  -Development of simple techniques for measuring or estimating plasma
  potentials.

- Characterization and understanding of plasma-surface interactions.

  -Improved understanding of adsorption-desorption phenomena in plasma
  environments.

  -Improved understanding of radical recombination at surfaces to form
  stable molecules.

  -Improved understanding of how bombardment of surfaces with energetic
  particles (ions, electrons, photons) enhances the rates of chemical
  reactions.

  -Improved understanding of the mechanisms of chemical reactions
  taking place at surfaces.

- Understanding how material properties relate to the plasma conditions
  present during their formation.

Applied Research and Engineering Needs

- Continued improvement in plasma-assisted etching technology for VLSIC
  silicon devices.

  -Improved etch selectivity with respect to mask and substrate
  materials to allow tighter line width control.

  -Improved in-process diagnostic tools.

  -Improved reactor designs leading to better uniformity and throughput.

- Wider application of plasma-assisted etching to solid-state device fabrication other than silicon integrated circuits.

  -Development of specific etching gases to meet the needs of other solid-state device technologies (e.g., for etching NiFe alloys, noble metals, and electro-optic materials).

- Improved reproducibility and uniformity for present plasma-enhanced CVD processes.

- Development of plasma-enhanced CVD processes to produce "active" dielectrics (e.g., for gate insulator applications in MOS-VLSIC).

- Refinement of processes for the deposition of hydrogenated amorphous silicon.

  -Better control of impurity incorporation.

  -Better control of microstructure.

  -Higher throughput.

- Extension of plasma-enhanced CVD to other device technologies.

- Correlation of film properties with plasma parameters for plasma-enhanced CVD.

- Assessment of potential applications where the unique properties of plasma polymerized films might be used advantageously.

APPENDIX A

GLOSSARY

Biot Number: A dimensionless number characterizing heat transfer between a fluid and a solid $(Bi = \frac{hL}{k})$.

Cold Plasma: A plasma where the electrons, ions and neutral gas phase particles are far from thermal equilibrium.

Conventional Plasma Spraying (CPS): Plasma spray deposition under atmospheric pressure conditions.

CVD: An abbreviation for "Chemical Vapor Deposition." CVD is a process whereby a coating is formed from constituents which are carried in the gas phase to the vicinity of the substrates where deposition takes place.

Directionally Solidified Eutectic Alloys: Controlled solidification to give an aligned eutectic structure; the heat flow is controlled so as to achieve a planar solid/liquid interface.

DRI (Direct Reduced Iron): Direct conversion of high purity iron ore into usable iron obviating the need for a blast furnace.

Dry Etching: Refers to all etching reactions where the etch product enters the gas phase.*

Electroslag Remelt: Electrodes are remelted where the molten droplets travel through a slag layer for refining purposes.

Free Radical: This term formally means particles with one unpaired electron. In this report, however, it is used synonymously with the term "reactive intermediate."

Glow Discharge (Discharge, Gas Discharge): In this report, the term glow discharge is used to imply a partially ionized gas (cold plasma) consisting of approximately equal numbers of positive and negative charges, and a different number of various types of neutral molecules.

HIP (Hot Isostatic Pressing): Consolidation of powder particles under the simultaneous influence of temperature and hydrostatic pressure.

Hollow Cathode: Hollow cathode in a plasma torch so that powders can be injected along the plasma jet axis.

Hot-topping: Insulating compound placed on top of a liquid reservoir during casting to ensure the presence of liquid to feed the casting.

IC: Integrated circuit.

Ion Plating: A deposition technique where a growing film is bombarded with energetic ions.

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Laser Doppler Anenometry: A diagnostic technique to measure velocity profiles of particulates entrained in gas streams.

LEED: An abbreviation for "Ultra-High Vacuum" which implies pressures below 10^{-9} Torr.

LPPD (Low Pressure Plasma Deposition): The plasma spraying deposition process as carried out in a reduced pressure (40-80 Torr) environment.

Magnetron Sputtering: A sputter deposition technique where cross magnetic and electric fields are used to modify the plasma.

Near-Net-Shape Components: Production of parts which require minimum machining operations to use as a finished component.

Nontransferred Arc: The arc is constrained within the plasma generator; there is no electrical connection (arc) to the workpiece.

Nusselts Number: A dimensionless number characterizing heat transfer across an interface ($Nu = \frac{hL}{k}$).

Organometallic Precursors: Organic compound that is the vehicle for introducing metallic species in the vapor phase either for chemical or physical vapor deposition techniques.

PACVD: An abbreviation for "Plasma-Assisted Chemical Vapor Deposition." PACVD is a process whereby a glow discharge plasma is used to promote CVD. (PACVD is sometimes called PECVD which means "Plasma-Enchanced Chemical Vapor Deposition.")

Pilot Discharge: Method for producing an initial arc or plasma discharge.

Plasma-Assisted Etching: Refers to all chemical etching reactions which occur in a plasma environment.*

Plasma Consolidation: Same as "Plasma Spray Deposition." The deposit is built up to form near net shape structures. The substrate may be removed by machining or etched away later.

Plasma Etching: Use of this term depends upon the author. It can apply to any or all of the previously defined processes. It often refers to chemical etching in the absence of ion bombardment. Sometimes it means that the etching reaction is not taking place at the powered electrode.*

Plasma Induction Furnace: A high frequency alternating magnetic field is used to inductively heat and maintain a plasma.

Plasma Polymerization: A process whereby a plasma is used to enhance a polymerization reaction.

Plasma Reactor: A general term used for process equipment that uses the plasma gases as a heat source or reactants for purposes of melting, purification, extraction, reduction or synthesis of materials.

Plasma Spray Deposition: Processes in which a material is introduced into the plasma jet, melted and subsequently deposited on a substrate. Though wire or rod feed have been used, powder injection is the most common method used for introduction of the material to be sprayed into the plasma jet.

Plasma Synthesis: The use of plasma as a heat source for purposes of chemical synthesis. The reactant gases may be used for the generation of the plasma itself or introduced later depending on the process.

Plasma Transferred Arc Deposition: Plasma spray deposition process with an arc transferred to the substrate.

Powder Metallurgy (P/M): A manufacturing process where the starting material is in powder form which is subsequently consolidated (mechanically) and sintered.

Rapid Quenching: Rapid cooling (10^3 K/s and higher) of material from the liquid to the solid state.

Rarefied Plasmas: A low density plasma, with large mean free path for the active species.*

Reactive Ion Etching: Refers to etching reactions which occur at the powered electrode in plasma environment.

Reynolds Number: A dimensionless number; ratio of inertial forces to viscous forces in fluid flow problems ($\frac{\rho VD}{\mu}$).

RSP (Rapid Solidification Processes): Solidification in which the cooling rate is approximately 10^3 K/s and higher.

Skull Casting (also called shell casting): Method for making hollow casting by draining the liquid metal after a thin shell has solidified.

Splat Cooling: Thin droplets are impacted on a substrate. The resulting thin splat undergoes rapid solidification.

Sputter Deposition: A process whereby material is physically sputtered from a target and subsequently deposited onto a substrate.

Sputter Etching: A process where "physical sputtering" is used to remove material from a surface.

Superalloys: Group of alloys characterized by excellent metallurgical stability at elevated temperatures, and hence use for high-temperature applications. The major constituent is either Fe, Co or Ni.

Superheat: "Superheat" refers to the temperature of a material in its liquid state; measured as the temperature above its melting point.

Supersaturated Solution: A solution in which the amount of dissolved solute exceeds the equilibrium value.

Thermal Pinch: A constriction in the confined plasma jet.

Transferred Arc: An arc is struck between the workplace and the electrode of the plas a torch.

Transport Properties: Physical properties of fluids that effect its flow, i.e., viscosity, density, thermal conductivity.

UHV: An abbreviation for "Ultra-High Vacuum" which implies pressures below 10^{-9} Torr.

UPS: An abbreviation for the analytical technique called "ultra-violet photo-electron spectroscopy." Ultra-violet light is used to produce electrons of characteristic energies which are then analyzed.

Vacuum Plasma Spraying (VPS): Plasma spray deposition process as carried out in a reduced pressure (40-80 Torr) environment. See LPPD.

VAR (Vacuum Arc Remelting): An arc is used to remelt one or both electrodes (in vacuum) for refining purposes.

VIM (Vacuum Induction Melting): Induction melting carrie   : under vacuum.

VLSI: Very Large Scale Integration

XPS: An abbreviation for the analytical technique called "x-ray photo-electron spectroscupy." The technique is also called ESCA, i.e., "electron spectroscopy for chemical analysis." X-rays are used to produce electrons of characteristic energies which are then analyzed.

*Terminology in this area is confusing and frequently non-descriptive. It would be best if one term were used to describe all etching processes which occur in a plasma environment, e.g., plasma-assisted etching.

LIST OF SYMBOLS

A	=	area covered by splatted particle
A_n	=	nozzle cross-sectional area
C	=	specific heat capacity at constant pressure
C_D	=	drag coefficient
d	=	splat diameter
D	=	particle diameter
h	=	heat transfer coefficient
k	=	thermal conductivity
M	=	gas mass flow rate
Ma	=	Mach number
Nu	=	Nusselt number
P_i	=	pressure in arc gas chamber
P_o	=	ambient pressure
p	=	$P_i - P_o$
Pr	=	Prandtl number
r	=	radial distance
Re	=	Reynolds number
S	=	thickness of splatted particle
t	=	time
T	=	temperature
V	=	velocity
m	=	ratio of splat diameter to original particle diameter, d/D
η	=	dynamic viscosity
ν	=	kinematic viscosity
ρ	=	density

Subscripts:

avg	=	properties calculated at arithmetic mean temperature
d	=	deposit
g	=	plasma gas
p	=	particle
S	=	particle surface
Sub	=	substrate

APPENDIX B

CURRICULA VITAE OF COMMITTEE
MEMBERS

MERTON C. FLEMINGS, a member of the National Academy of Engineering, holds a Sc.D. (in metallurgy) from Massachusetts Institute of Technology. Professor Flemings has been a faculty member at MIT since 1956 and Director of the Materials Processing Center since 1979. He is the co-author of 170 papers and two books in the field of materials processing and solidification science.

JULIAN SZEKELY is a Professor of Materials Engineering at Massachusetts Institute of Technology. Dr. Szekely received his B.Sc., Ph.D., and D.Sc. (Eng.) degrees from Imperial College, University of London, England. He taught at Imperial College and at the State University of New York at Buffalo before taking up his current position. His main research interests are in heat transfer, fluid flow, and mass transfer in materials processing operations, with emphasis on electromagnetically driven flow systems. Professor Szekely is a member of the National Academy of Engineering.

NOEL JARRETT received his Master of Science degree from the University of Michigan. At present he holds the position of Assistant Director, Metal Products, Alcoa Labs, Aluminum Company of America, and is active in a number of professional societies. Mr. Jarrett is a member of the National Academy of Engineering.

BERNARD H. KEAR is scientific advisor at the Exxon Research and Engineering Company. His previous professional affiliation was with the United Technologies Research Center, where he served as Senior Consulting Scientist. Dr. Kear received his Ph.D. (1957) and D.Sc. (1970) degrees from Birmingham University. A member of the National Academy of Engineering, Dr. Kear's research has been in alloy design and processing of superalloys and surface modification of materials.

EMIL PFENDER holds a Diploma degree in physics and a D.Eng. (Electrical Engineering) from the University of Stuttgart, Germany. He has been a Professor of Mechanical Engineering at the University of Minnesota since 1967, where he is also in charge of The High Temperature Laboratory. Professor Pfender has authored and co-authored more than 120 papers in the areas of plasma chemistry and processing, arc technology and plasma heat transfer.

EARL THOMPSON holds a D.Sc. degree (Materials Science) from the University of Virginia. He is at present manager of materials science at United Technologies Research Center. His research includes work in high-temperature alloys, composite materials, rapidly solidified alloys, and processing of metals by lasers.

PHILIP H. WILKS is President of Plasma Materials Incorporated. He received a Ph.D. (Inorganic Chemistry) from the University of Pittsburgh and, prior to his present affiliation, worked for the General Electric Company, Westinghouse Corporation, and Humphreys Corporation. His expertise is in the area of plasma chemistry, and high-temperature materials.

DIRAN APELIAN received a Sc.D. (Materials Science) from Massachusetts Institute of Technology, and is now Professor and Head, Department of Materials Engineering at Drexel University. Professor Apelian is active in several professional societies, and his research includes work in solidification processing, liquid metal filtration, development of rapid-cycle casting technologies, and low-pressure plasma processing.

CYRIL JOSEPH MOGAB is currently Head, III-V Processing Technology Department at AT&T-Bell Laboratories. Holder of a Sc.D. (Ceramics) from Massachusetts Institute of Technology, Dr. Mogab served as an assistant professor at MIT prior to joining Bell Labs in 1970. His research has been in thin films, plasma etching and deposition, and electronic materials.

WARD ROMAN received a Ph.D. (Mechanical Engineering) from Ohio State University. His professional experience includes work at the Aerospace Research Laboratory, Wright Patterson Air Force Base, where he was employed as Director Plasma Technology; his present position at United Technologies Research Center is Senior Consulting Engineer. Dr. Roman's expertise is in the fields of thermal plasma technology, plasma spray coatings, high-temperature diagnostic techniques, plasma chemistry and chemical lasers.

HAROLD F. WINTERS is a member of the Physics Research staff at the IBM Research Lab, IBM Company, San Jose, California. He received a Ph.D. (Physics) from Washington State University and since graduation has done research in the fields of surface, vacuum, and electron physics and ion bombardment of solid surfaces.

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